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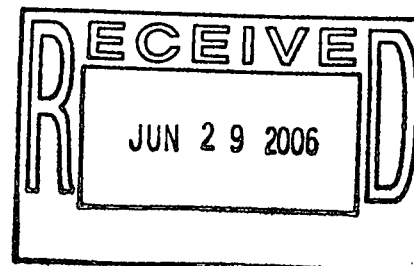
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Final Report
February 1984

Chemical Attenuation Rates, Coefficients, and Constants in Leachate Migration

Volume 1: A Critical Review

Prepared by
Battelle, Pacific Northwest Laboratories
Richland, Washington

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Chemical Attenuation Rates, Coefficients, and
Constants in Leachate Migration
Volume 1: A Critical Review

EA-3356, Volume 1
Research Project 2198-1

Final Report, February 1984

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Prepared by
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ABSTRACT

This project was initiated in August, 1982 to compile and critically evaluate the data from existing literature on chemical (precipitation/dissolution and adsorption/desorption) and biological (methylation and alkylation) attenuation mechanisms that affect aqueous concentrations of elements and thus their geochemical behavior in the subsurface environment. Elements considered for chemical mechanisms were Al, Sb, As, Ba, Be, B, Cd, Cr, Cu, F, Fe, Pb, Mn, Hg, Mo, Ni, Se, Na, S, V and Zn. The review of biological mechanisms focused on microbiological alkylation of As, Hg, and Se. This report (Volume 1) deals with a critical review of these chemical and biological attenuation mechanisms, whereas Volume 2 "Attenuation Rates, Coefficients and Constants in Leachate Migration: An Annotated Bibliography" lists over 350 references and abstracts pertaining to this topic.

The information discussed in the report for each element includes 1) thermodynamic predictions of stable solid and solution species which may be present in the utility waste environment, 2) observed solubility-controlling solids, and 3) a summary of the effect of different geochemical factors that control adsorption/desorption. The definitions of constants and examples of their use in calculating attenuation (Section 2), along with extensive tables for thermodynamic equilibrium constants and adsorption/desorption constants for each element are an important aspect of this report. Because quantitative information on alkylation is not available, calculations were made under assumed environmental conditions to display and assess the importance of subsurface alkylation reactions.

As a result of this first phase, it was learned that adequate data to make quantitative estimates of the rates of chemical attenuation in the subsurface environment exist for only a few solutes. Precipitation/dissolution and adsorption/desorption were found to be the most important chemical attenuation mechanisms and the attenuation rates are expected to differ according to the chemical element and the composition of the geologic material.

EPRI PERSPECTIVE

PROJECT DESCRIPTION

RP2198 was initiated to compile and develop new quantitative data on chemical attenuation of inorganic elements in the subsurface environment. Phase I of the research was devoted to compiling and reviewing the data from literature. Phase II of the research will be devoted to the development of new quantitative data. Study of geochemical interactions between soils and groundwaters is one essential part of EPRI's Solid Waste Environmental Studies project (RP2485) aimed at developing methods of predicting the environmental fate of leachates. In Phase I, the researchers reviewed the literature on chemical attenuation to establish the applicability of data to waste disposal systems on the basis and adequacy of experimental procedures, degree of characterization, and data interpretation. Quantitative data summaries for chemical and biological attenuation mechanisms (precipitation/dissolution, adsorption/desorption, alkylation and methylation) are given in Volume 1. An annotated bibliography is in Volume 2 of this report.

PROJECT OBJECTIVES

The objectives for Phase I of this project (RP2198-1) were to compile and evaluate information on chemical attenuation of inorganic solutes and to design laboratory and field experiments to obtain additional data on chemical attenuation of solutes in the geologic environments.

PROJECT RESULTS

This Phase I report has successfully delivered a comprehensive compilation of data on chemical attenuation rates and on constants and coefficients for 21 inorganic elements (Al, Sb, As, Ba, Be, B, Cd, Cr, Cu, F, Fe, Pb, Mn, Hg, Mo, Ni, Se, Na, S, V, Zn). The research provided the data on which to base laboratory and field experiments being conducted in the Phase II research now under way in EPRI RP2485. This report provides a unique collection of information compiled from an extensive literature search and is to be used by the utility environmental staff who deal with the issue of solid residue disposal and its effect on groundwater. This report (Volume 1) is expected to be an important contribution to the subject of chemical

attenuation in soils. Volume 2, the annotated bibliography, contains about 350 pertinent publications that provide the data in Volume 1.

The important results from Phase I research are summarized below:

1. For only a few solutes, adequate data exist for making quantitative estimates for the rates of chemical attenuation in the subsurface environment.
2. Chemical attenuation rates should be expected to differ according to the chemical element and the composition of the geological environments.
3. Precipitation/dissolution and adsorption/desorption are found to be the most important chemical attenuation mechanisms.
4. Precipitation/dissolution, although recognized to be important, has not been adequately studied, especially for trace elements.
5. Because of similarity in geochemical behavior, many elements can be brought together and studied as a group. Such generalized groupings can lead to more efficient research.

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Energy Analysis and Environment Division

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SUMMARY

Literature data applicable to chemical attenuation in the subsurface environment of inorganic species contained in utility wastes were compiled and critically evaluated for their usefulness in predicting the geochemical behavior of these inorganic species. Although biological attenuation mechanisms were also reviewed, chemical attenuation mechanisms were judged to be more important for a majority of the chemical species. Chemical attenuation refers to reactions that occur between leachate constituents and geologic material, which change the distribution and concentration of the inorganic species in the pore waters and hence their mobility. These reactions can be grouped under two headings: precipitation/dissolution and adsorption/desorption. Therefore, the review was focused on establishing the effects of key hydrochemical and geologic factors on precipitation/dissolution and adsorption/desorption mechanisms.

The information discussed in the report for each element includes 1) thermodynamic predictions of stable solid and solution species which may be present in the utility waste environment, 2) observed solubility-controlling solids, and 3) a summary of the effect of different geochemical factors that control adsorption/desorption. The definitions of constants and examples of their use in calculating attenuation (Section 2) along with extensive tables for thermodynamic equilibrium constants and adsorption/desorption constants for each element are an important aspect of this report. Important findings from the review are summarized below.

PRECIPITATION/DISSOLUTION

The nature of the aqueous species is important in understanding both precipitation/dissolution and adsorption/desorption reactions. As a general rule, complexed species increase the solubility of solid phases and they are not adsorbed by mineral surfaces. Thus, aqueous complexation may enhance mobility. The aqueous species were predicted from selected thermodynamic data for each element under conditions anticipated in the utility waste environment. The speciation calculations reported in the text were made under an assumed groundwater composition ($\text{SO}_4^{2-} = \text{Cl}^- = 10^{-3} \text{ M}$, $\text{NO}_3^- = \text{F}^- = 10^{-4} \text{ M}$, $\text{Br}^- = \text{I}^- = 10^{-5} \text{ M}$, $\text{pCO}_2 = 10^{-3.52}$) and a range in pH and E^{H} . However, the thermodynamic data can be used to calculate speciation under other

conditions as well. The predicted important aqueous species for different elements are reported in Table 1. This table is provided only as an example of important solution species for the elements. Additional details are elaborated in the text. Table 1 does show that some of the elements are 1) cationic (e.g., Cd, Pb, Ni, Zn) and that these elements may exist in utility waste environment as complexes with differing charge characteristics, 2) anionic (e.g., F^- , MoO_4^{2-}), and 3) redox sensitive (e.g., Cr, Se). This information was useful in grouping the elements based on the similarities in their attenuation behavior.

Precipitation of solid phases is an important attenuation mechanism. In cases where the solid phase of an element is present or can form in substrata and rates of precipitation/dissolution are rapid, the equilibrium solution concentration is controlled by the solubility of the solid phase even though adsorption/desorption reactions may be occurring. Therefore, the existing thermochemical literature was reviewed to identify the most stable phases of different elements that may form in the geologic environment. These stable phases were then used to predict, based on available thermodynamic data, the equilibrium concentrations for the elements. These predicted concentrations should only be used as a guide in cases where the predictions have not yet been validated. Where possible, uncertainties and large variabilities were identified in the existing thermodynamic data.

In general, the review indicated that precipitation/dissolution, although recognized to be important, has not been adequately studied, especially for trace elements. Except for a few elements (Al, Fe, Mn), either the evidence for the existence of solubility-controlling solid phases is indirect (comparison of ion activity products to solubility products) or their existence is postulated to explain observed adsorption behavior. The limited information, however, does suggest that a number of solid/mineral phases (Table 2) may control the aqueous concentrations of selected utility waste constituents in subsurface porewaters or groundwaters. This list will undoubtedly expand as research progresses.

Many of the solids [e.g., $BaSO_4$, $PbCO_3$, $Cr(OH)_3$] reported in Table 2 are particularly germane to the utility waste environment where sulfate, bicarbonate/carbonate, and hydroxide are dominant anions in the waste leachate. Hydroxide and carbonate solids are more soluble at low pH values. Therefore, these solid phases are important only in near neutral and alkaline geologic materials. Solubility-controlling hydroxide and carbonate solid phases of trace elements (e.g., Cd, Pb, Cu) are

Table S-1
IMPORTANT SOLUTION SPECIES OF ELEMENTS(a)

Element	Unaffected by Oxidation-Reduction(b)	Oxidizing Environment	Reducing Environment
Al	$Al^{3+}, AlSO_4^+, AlF^{2+}, Al(OH)_2^+, Al(OH)_3^0, Al(OH)_4^-$		
Sb		$Sb(OH)_6^-$	$Sb(OH)_3^0$
As		$H_2AsO_4^-, HASO_4^{2-}$	$H_3AsO_3^0, H_2AsO_3^-$
Ba	$Ba^{2+}, BaSO_4^0, BaCO_3^0$		
Be	$Be^{2+}, BeF^+, BeOH^+, Be(OH)_2^0, Be(OH)_3^-$		
B	$H_3BO_3^0, B(OH)_4^-$		
Cd	$Cd^{2+}, CdSO_4^0, CdCO_3^0$		
Cr		$HCrO_4^-, CrO_4^{2-}$	$Cr^{3+}, CrF^{2+}, CrOH^{2+}, Cr(OH)_3^0, Cr(OH)_4^-$
Cu		$Cu^{2+}, CuSO_4^0, Cu(OH)_2^0$	$Cu^+, CuCl_2^-, Cu(OH)_2^0$
F	$F^-, AlF_2^+, AlF^{2+}, AlF_3^0$		
Fe		$FeF^{2+}, Fe(OH)_2^+, Fe(OH)_3^0, Fe(OH)_4^-$	$Fe^{2+}, FeSO_4^0, Fe(OH)_4^-$
Pb	$Pb^{2+}, PbCO_3^0, Pb(CO_3)_2^{2-}$		
Mn	$Mn^{2+}, MnSO_4^0$		
Hg		$HgI_2^0, Hg(OH)_2^0, HgIOH^0$	Hg^0
Mo	MoO_4^{2-}		
Ni	$Ni^{2+}, NiHCO_3^+, NiSO_4^0$		
Se		SeO_4^{2-}	$HSeO_3^-, SeO_3^{2-}, HSe^-$
Na	Na^+		
SO ₄	$SO_4^{2-}, CaSO_4^0$		
V		$H_2VO_4^-, HVO_4^{2-}$	$VO_2^{2+}, V(OH)_2^+, V(OH)_3^0$
Zn	$Zn^{2+}, ZnSO_4^0, ZnCO_3^0, Zn(CO_3)_2^{2-}$		

(a) This table should only be used as a guide, for details of stability fields of different species, see text; conditions assumed for this table included pH range 4 to 10, $SO_4^{2-} = Cl^- = 10^{-3} M$, $NO_3^- = F^- = 10^{-4} M$, $Br^- = I^- = 10^{-5} M$, $pCO_2(gas) = 10^{-3.52}$, $Na^+ = Ca^{2+} = K^+ = 10^{-3} M$, $Mg^{2+} = 10^{-4} M$.

(b) Some of these species (e.g. SO_4^{2-} , Pb, Mn) are redox sensitive, however extreme redox conditions, prevalent only in a limited number of cases, are required (e.g., at very reducing conditions (pe + pH < 4) S^{2-} is the dominant aqueous sulfur species and S^{2-} may form significant complexes with cations).

commonly observed in adsorption studies or in soils amended with wastes (such as sewage sludge), where trace elements were present in relatively high concentrations.

Precipitation is a primary attenuation mechanism for Fe, Al, and Mn; these elements form a variety of compounds which limit their concentrations in groundwaters to low levels. Crystalline and amorphous oxides of Fe are ubiquitous in geologic materials. Although confirmatory studies are needed, the available data suggest that formation of Fe containing solids [e.g., $FeMoO_4$, $NiFe_2O_4$, $Fe_2(SeO_3)_3$] may be a

Table S-2

SUMMARY OF IMPORTANT SOLUBILITY-CONTROLLING SOLIDS
REPORTED IN THE LITERATURE^(a)

Element	Observed/Predicted ^(b)	Speculated ^(c)
Al	$\text{Al}(\text{OH})_3$, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, AlOHSO_4 , Kaolinite, Montmorillonite	
As		FeAsO_4 , AsS or As_2S_3
Ba	BaSO_4	
Be		$\text{Be}(\text{OH})_2$
Cd	CdCO_3 , $\text{Cd}_3(\text{PO}_4)_2$	$(\text{Ca}, \text{Cd})\text{CO}_3$
Cr	$\text{Cr}(\text{OH})_3$	FeCr_2O_4
Cu	$\text{Cu}(\text{OH})_2$	$\text{Cu}_2(\text{PO}_4)_3$, $\text{Cu}_2(\text{OH})_2\text{CO}_3$
Fe	$\text{Fe}(\text{OH})_3$, $\text{Fe}_3(\text{OH})_8$, FeCO_3	
Hg	HgS	
Pb	$\text{Pb}(\text{OH})_2$, PbCO_3 , $\text{Pb}_3(\text{PO}_4)_2$, $\text{Pb}_4\text{O}(\text{PO}_4)_2$, $\text{Pb}_5(\text{PO}_4)_3\text{OH}$	
Mn	MnCO_3 , Mn-oxides	
Mo	PbMoO_4	FeMoO_4 , $\text{Fe}_2(\text{MoO}_4)_3$
Ni	NiS	NiFe_2O_4
Se		$\text{Fe}_2(\text{SeO}_3)_3$
S	CaSO_4 , $\text{Al}_4(\text{OH})_{10}\text{SO}_4 \cdot 5\text{H}_2\text{O}$, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$	
V		$\text{Fe}_2(\text{VO}_3)_2$, $\text{VO}(\text{OH})_2 \cdot \text{H}_2\text{O}$
Zn	$\text{Zn}(\text{OH})_2$, ZnCO_3 , ZnSiO_4	ZnFe_2O_4

(a) All solid phases are not expected in all environments, e.g. hydroxides and carbonate solids are expected only under near neutral to alkline conditions and sulfides (e.g., HgS , NiS) are expected only under very reducing conditions; for details see text.

(b) Solids whose presence has been established through physical observations of geologic materials or through similarities in ion activity products with the solubility products.

(c) The formation and presence of Fe containing compounds is speculated primarily based on adsorption experiments or observed association of other elements with iron oxides.

significant chemical attenuation mechanism for both cationic (e.g., Cr, Ni, Zn) and anionic (As, Cr, Mo, Se, V) constituents in diverse hydrochemical environments. Under reducing conditions where S^{2-} exists, precipitation of sulfides (e.g., NiS, PbS) is expected to be an important chemical attenuation mechanism.

Because of expected low concentrations of trace elements in the utility waste leachates, precipitation of solid solutions $[(Cr, Fe)(OH)_3, (Cd, Ca)CO_3]$ rather than discrete solids may be of greater significance. Solid solutions generally have lower solubilities than the discrete end member solid phases. However, quantitative information on kinetics of precipitation and solubility products for these solid solutions is unavailable.

ADSORPTION/DESORPTION

The review has shown that adsorption is a complex function of 1) the geologic matrix and 2) the hydrogeochemical environment (Table 3). For many of the waste constituents, research consistently alludes to the importance of specific adsorption at low trace element concentrations. Hydrous oxides of Al, Fe, and Mn, amorphous aluminosilicates, and organic material appear as important specific adsorbents and thus exist as coatings on clay sized materials in soil and subsoil and give rise to the high adsorption capacity commonly observed for this size fraction. Layer lattice silicates account for most of the cation exchange capacity. The above adsorbents represent the most significant adsorption surfaces in geologic materials underlying utility waste sites.

Hydrochemical conditions influence adsorption by: 1) controlling ion speciation, 2) providing ions that compete for adsorption sites, and 3) affecting the net surface charge on amphoteric adsorbents (e.g., Fe and Mn oxides, amorphous aluminosilicates) and affecting base saturation and exchangeable acidity of cation exchange materials. Element speciation (Table 1) is controlled primarily by solution pH, EH, and ion composition. Research indicates that for the most part, only uncomplexed ions (e.g., Cd^{2+}) rather than complexed ions (e.g., $CdSO_4^0$, $CdCO_3^0$) are adsorbed. Thus, hydrochemical conditions in leachate or ground water which favor complexation will reduce adsorption. Similarly, solution redox potential controls the valence of redox sensitive elements. For some elements (e.g., Cr) different valence states exhibit markedly different adsorption behavior. In addition to affecting solution speciation of cations via complexation, major leachate anions (e.g., SO_4^{2-}) may compete for available adsorption sites with utility waste contaminants of similar chemical behavior (e.g., SeO_4^{2-} , CrO_4^{2-}), thus reducing the adsorption of each

Table S-3

SOME IMPORTANT FACTORS REPORTED IN LITERATURE THAT AFFECT ADSORPTION^(a)

Element	Geologic Matrix					Hydrochemical Environment			
	Most Important Adsorbents					Important Solution Variables			
	Fe-Oxide	Mn-Oxides	Clays	Amorphous Aluminosilicates	Org C	pH	Eh	Complexing Ions	Competing Ions
Al			X	X	X	X		X	
Sb									
As	X					X	X	X	
Ba			X					X	X
Be									
B	X		X	X		X		X	
Cd	X	X	X			X			X
Cr	X	X	X		X	X	X	X	X
Cu	X	X	X		X	X	X	X	X
F	X			X		X		X	X
Fe	X	X			X	X	X	X	X
Pb	X	X	X			X		X	X
Mn		X				X	X	X	X
Hg	X	X			X	X	X	X	
Mo	X			X		X			
Ni	X	X				X		X	X
Se	X			X		X	X		X
Na			X						X
SO ₄	X			X		X	X	X	X
V									
Zn	X					X		X	X

(a) X indicates reported in literature whereas blank space indicates no data.

individual constituent. Most specific adsorbents (e.g., Fe, Mn oxides, amorphous aluminosilicates) have a pH-dependent surface charge. These constituents are positively charged at pH values below their point of zero charge (PZC), and negatively charged above; the PZC is a unique characteristic of each adsorbent. Thus, decreasing groundwater pH increases positive charge and favors anion retention, while increasing pH encourages cation adsorption.

Though considerable descriptive and qualitative information is available for some elements, this review has clearly shown that a capability does not exist to predict quantitatively the adsorption behavior based upon mineralogy and groundwater composition. This lack of predictive capability stems from the unavailability of 1) a systematic understanding and generalized numerical approach to integrate the effects of critical hydrochemical parameters (Table 3) on adsorption, 2) methods to quantify the contribution of individual adsorbents in a heterogeneous geologic matrix, and 3) quantitative mechanistic adsorption data devoid of precipitation effects. Many adsorption studies reported in the literature use high elemental concentrations such that the adsorption results were complicated by precipitation of solid phases. In spite of the shortcomings in available information, this review has shown that useful generalizations and broad groupings of elements with similar geochemical behavior can be made.

The cationic elements (Table 1) are adsorbed specifically and by ion exchange. With the exception of Na and Ba, the specific adsorption process predominates for most utility waste constituents at lower environmental concentrations ($<10^{-5}$ M). Ion exchange occurs when the specific adsorption capacity is exceeded. Sodium and barium are retained primarily through ion exchange. The affinity of specifically adsorbed cations for hydrous oxide decreases in the following order, $Pb > Cu > Zn > Ni > Cd$. Some cationic elements, notably Cu and Hg, are strongly complexed by particulate organic materials. The adsorption of most cationic elements increases with an increase in pH. Increasing adsorption with pH results from hydrolysis of the cations and decrease in positive charge of amphoteric adsorbents. Thus, the cations are significantly more mobile under acidic than basic conditions.

Ligands (e.g., Cl^- , SO_4^{2-} , F^-) that form stable aqueous complexes with cations (e.g., Pb^{2+} , Cu^{2+} , Ni^{2+} , Cd^{2+} , Hg^{2+}) reduce free cation activity and hence element adsorption. Chloride complexes of Hg are most significant in this respect. The presence of macro ions (e.g., Ca^{2+} , Na^+) and specifically adsorbing ions (e.g., Cu, Zn, Cd) in solution also tend to reduce adsorption through competition for cation exchange sites and specific adsorption sites, respectively.

The oxyanions (MoO_4^{2-} , CrO_4^{2-} , SeO_3^{2-} , SeO_4^{2-} , AsO_3^{3-} , AsO_4^{3-} , SO_4^{2-}) (Table 1) are adsorbed specifically by mineralogic constituents which carry positive charge. The adsorption of oxyanions is strongly pH dependent with maximum adsorption occurring under acidic conditions where adsorbents that show amphoteric behavior (iron and aluminum oxides, amorphous aluminosilicates) are positively charged. The adsorptivity of oxyanions decreases in the following general order $As > Cr > Mo > Se \approx$

SO₄. Boron exhibits contrasting behavior and is most strongly adsorbed at higher pH (8.5 to 10) by amorphous aluminosilicates, and Al and Fe oxides. Aqueous complexes of oxyanions with cationic macro elements (e.g., CaCrO₄) may reduce specific adsorption of oxyanions because the complexes are weakly adsorbed. However, positively charged complexes [e.g., CaB(OH)₄⁺] may be retained in subsoil by ion exchange. The presence of high levels of SO₄²⁻ in leachates may decrease the adsorption of some oxyanions (e.g., CrO₄²⁻, MoO₄²⁻, SeO₃²⁻, SeO₄²⁻) by strong competition for available adsorption sites.

CONCLUSIONS

Based on this review of chemical attenuation mechanisms applicable to the utility waste environment, the following general conclusions can be drawn.

- Chemical attenuation mechanisms were judged to be more important than biological attenuation mechanisms for a majority of the species.
- Chemical mechanisms fall under two headings--precipitation/dissolution and adsorption/desorption. These mechanisms are affected by many factors related to the geologic matrix and hydrochemical environment (e.g., pH, E^H, complexing ligands, competing ions, nature of adsorbents).
- Precipitation/dissolution, although recognized to be important, has not been adequately studied. However, available data suggest that:
 - Precipitation is a primary attenuation mechanism for Fe, Al, and Mn.
 - Solubility-controlling carbonate and hydroxide solid phases of trace elements (e.g., Cd, Pb, Cr, Cu) have been observed in alkaline conditions.
 - Formation of iron containing solids may be an important chemical attenuation mechanism for both cationic (e.g., Cr, Ni, Zn) and anionic (As, Cr, Mo, Se, V) elements.
 - Precipitation of solid solutions [e.g., (Fe,Cr)(OH)₃, (Ca,Cd)CO₃] is expected to be a very important chemical attenuation mechanism.
 - Reliable thermodynamic data are not available for several important solid phases and aqueous species.
- Quantitative predictions of chemical attenuation rates based upon mineralogy and groundwater composition cannot be made because only descriptive and qualitative information are available for adsorption/desorption mechanisms. From the available data we conclude that:
 - Only uncomplexed (e.g., Cd²⁺) rather than complexed ions (e.g., CdSO₄⁰, CdCO₃⁰) are adsorbed.

- Hydrous oxides of Al, Fe, and Mn, amorphous aluminosilicates, and organic carbon are important specific adsorbents.
- Aqueous species influence adsorption; anions such as F^- , CrO_4^{2-} , SO_4^{2-} are adsorbed strongly at low pH, while adsorption of cations such as Cd^{2+} , Cu^{2+} , Zn^{2+} increases with the increase in pH.
- For most elements, specific adsorption predominates at lower environmental concentrations of elements ($<10^{-5}$ M).
- Competing ions and complexing ligands generally reduce adsorption.
- Quantitative mechanistic adsorption data devoid of precipitation effects are not yet available.

Section 1

INTRODUCTION

During the generation of electricity, conventional coal-fired power plants produce by-products requiring storage and disposal. These by-products (fly ash, bottom ash, flue gas desulfurization (FGD) sludges, scrubber sludges) differ in their chemical composition, primarily because of the chemical composition of the coal and processes used. Regardless of the chemical differences, virtually all of these wastes contain water-soluble inorganic components of environmental concern. The percolates from disposal utility wastes may contaminate surface and ground-water supplies. To determine the potential for surface and groundwater pollution arising from waste disposal at a given site, one needs to understand: 1) the waste characteristics and environmental conditions as they influence leachate generation, and 2) the subsequent interaction of the leachate with soils/geologic materials as these interactions influence the rate of movement or attenuation of leachate constituents. Primary physicochemical attenuation mechanisms include precipitation/dissolution, adsorption/desorption, and microbiological activity. Although dispersion and dilution can also be important physical processes affecting constituent attenuation during hydrologic transport, this report discusses only chemical and biological mechanisms.

Studies to evaluate attenuation of constituents on a site-specific basis would be prohibitively expensive, particularly as the results for one site cannot be reasonably extrapolated to other sites. Therefore, a more cost-effective approach, where quantitative data can be used to develop a mechanistic understanding and evaluation of attenuation processes of waste constituents, is needed. This mechanistic understanding must include: 1) information on solubility-controlling solids that may be present or form in the geologic environment, 2) kinetics of precipitation/dissolution of solids, 3) accurate thermochemical data for important aqueous and solid species, 4) a generalized numerical approach to integrate the effects of critical hydrochemical parameters on adsorption, 5) methods to quantify the contribution of individual adsorbents in a heterogeneous matrix, and 6) quantitative mechanistic adsorption data devoid of precipitation effects.

Considerable quantitative data have been generated through studies with soils for elements that are either of agronomic or industrial importance. Many of these elements are also important in fossil-fuel wastes. However, many of these studies were: 1) not directed toward utility waste disposal, 2) narrow in focus (e.g., addressing a single soil or a narrow pH range), and 3) site specific. As a result, a critical review of the available data is needed to identify useful information applicable to quantifying geochemical behavior of elements (Table 1-1) that may be present in leachates from utility wastes.

This report documents efforts to compile and critically evaluate existing data on attenuation coefficients and constants applicable to utility waste leachate

Table 1-1
ELEMENTS FOR ATTENUATION LITERATURE REVIEW

Element	Symbol	Primary Species		Redox Sensitive
		Cationic	Anionic	
Aluminum	Al	X		
Antimony	Sb		X	X
Arsenic	As		X	X
Barium	Ba	X		
Beryllium	Be	X		
Boron	B		X	
Cadmium	Cd	X		
Chromium	Cr	X	X	X
Copper	Cu	X		X
Fluoride	F		X	
Iron	Fe	X		X
Lead	Pb	X		X
Manganese	Mn	X		X
Mercury	Hg	X		X
Molybdenum	Mo		X	X
Nickel	Ni	X		
Selenium	Se		X	X
Sodium	Na	X		
Sulfate	SO ₄		X	X
Vanadium	V	X	X	X
Zinc	Zn	X		

migration. A follow-on project (currently underway) will develop additionally needed data identified through this critical review. Ultimately these projects will provide EPRI and its member utilities with an improved understanding of the chemical attenuation mechanisms controlling leachate migration.

This report is organized into sections and appendices. Section 2 addresses the procedures of compiling, reviewing, evaluating, and tabulating the useful data along with the definitions of different constants. Sections 3 to 23 discuss elemental behavior (Table 1-1). This discussion of elemental behavior includes a brief abstract, thermodynamic data-based predictions of the relative stability of solid and aqueous species, observed or hypothesized solubility controls in surficial geochemical environments and adsorption/desorption reactions in soils/subsoils and sediments or on geologic materials. Certain subtleties of precipitation/dissolution and adsorption/desorption mechanisms need to be understood to determine the mechanisms controlling solution concentrations. If the solid phase of an element is present in the geologic material or if it can precipitate and if the rate of precipitation/dissolution is rapid, the solution concentration of this element will be governed solely by the solubility of the solid phases even though adsorption/desorption reactions may be occurring. When more than one solid phase of an element can precipitate or dissolve, the most soluble phase usually controls the solubility and the resulting activity of the ionic species. In the absence of a solid phase, adsorption/desorption reactions will control the solution concentrations. Adsorption constant data compiled during the course of this study are presented in the text (Sections 3 through 23) whereas thermochemical data are presented in Appendix A. Because only limited information on subsurface biological attenuation is available, a short review of this mechanism is presented in Appendix B.

Section 2

DESCRIPTION OF CHEMICAL ATTENUATION REACTIONS AND CONSTANTS

Chemical attenuation refers to chemical reactions occurring between leachate constituents and geologic material that change the distribution and concentration of the species in pore waters and hence their mobility. These reactions can be grouped under two headings: precipitation/dissolution and adsorption/desorption. This literature review was designed to provide an understanding of these chemical attenuation mechanisms affecting leachate migration from utility wastes. To ensure that the compiled information was applicable to utility waste disposal issues, research results from a number of sources were evaluated. These results included thermodynamic data on elements pertinent to utility wastes as well as precipitation/dissolution and adsorption/desorption reactions of these elements in geologic materials. Discussed in this section are general and specific review procedures, definitions and descriptions of attenuation constants, and an example to illustrate the use of attenuation constants to predict equilibrium elemental concentrations in pore water contacting geologic materials.

GENERAL REVIEW PROCEDURES

In reviewing the literature, procedures were established for compiling, reviewing, evaluating and tabulating the data for both the thermodynamic data and the adsorption/desorption data. As outlined below, these procedures varied slightly depending on the available information and the degree of detail. For example, criteria were mainly applied to elements where large amounts of data exist. For those elements where information is sparse, criteria were applied subjectively to eliminate data which were totally unacceptable. In some cases, data which did not pass the evaluation criteria were used to qualitatively assess element behavior and are cited in the written element review. All articles and publications that reported adsorption constants were tabulated, whereas in the case of thermodynamic data only one value for a given reaction was finally selected and tabulated from all available values.

THERMODYNAMIC EQUILIBRIUM CONSTANTS, DOMINANT AQUEOUS SPECIES, AND SOLUBILITY CONTROLLING SOLID PHASES

For many of the utility waste contaminants, thermodynamic data are included in the geochemical code MINTEQ* (Felmy et al. 1983), which uses the data base of WATEQ2 (Truesdell and Jones 1974, Ball et al. 1980). However, thermodynamic data for Be, Cr, Hg, Mo, Sb, Se, and V are not currently included in the model. As a result, data for these elements were reviewed and selected from the available literature (see Appendix A for tabulated data).

In selecting the appropriate thermodynamic data the following procedure was used: 1) compilation of data, 2) calculation of equilibrium constants, where needed, 3) selection of preliminary constants, 4) identification of important solid and solution species, and 5) tabulation of finally selected values. Data were compiled from major reviews** and recently published technical papers identified through a computer search of chemical abstracts. Thermodynamic equilibrium constants were tabulated from these references.

Equilibrium constants were calculated from several references such as Wagman et al. (1968, 1969, 1971) and Parker et al. (1971) that quote standard Gibbs free energies of formation (ΔG_f^0) for different species. However, to ensure the internal consistency of the thermodynamic data, ΔG_f^0 for ancillary species reported in Table 2-1 were used in these calculations. Most of these values are identical to those used by Krupka and Jenne (1982) in the WATEQ3 code. The values of the thermodynamic equilibrium constants (K^0) (Eq. 2-1) were calculated from ΔG_f^0 using Eqs. 2-2 and 2-3.



$$K^0 = \frac{(Z)^c}{(X)^a (Y)^b}$$

* MINTEQ is an equilibrium code and combines the best features of WATEQ4 and MINEQL. It has the capabilities of calculating 1) the saturation index of a given solid, 2) aqueous speciation, 3) mass balance from precipitation/dissolution reactions, and 4) the effect of adsorption reactions on aqueous speciation.

** Such as Sillen and Martell (1964, 1976), Wagman et al. (1968, 1969, 1971), Parker et al. (1971), Robie et al. (1978), Lindsay (1979), Smith and Martell (1976), Naumov et al. (1974), Baes and Mesmer (1976).

Table 2-1

ANCILLARY DATA USED IN THIS STUDY

Species	$\Delta G_{f,298}^0$ (kcal/mol)	Reference
H ₂ O(l)	-56.690	CODATA (1976)
OH ⁻	-37.604	CODATA (1976)
H ⁺	0	Wagman et al. (1968)
Ag ⁺	18.433	Wagman et al. (1968)
Al ³⁺	-116.9	Robie et al. (1978)
Al(OH) ₃ (gibbsite)	-275.03 ^a	May et al. (1979)
Ca ²⁺	-132.30	Parker et al. (1971)
Cl ⁻	-31.372	Wagman et al. (1968)
F ⁻	-67.34	CODATA (1976)
Fe ²⁺	-18.85	Wagman et al. (1969)
Fe ³⁺	-1.1	Wagman et al. (1969)
H ₄ SiO ₄ ^o	-312.55 ^b	ΔH : Robie et al. (1978) S: Wagman et al. (1968)
K ⁺	-67.51	CODATA (1976)
Mg ⁺²	-108.7	Parker et al. (1971)
Mn ⁺²	-54.5	Wagman et al. (1969)
Na ⁺	-62.593	Wagman et al. (1981)
SiO ₂ (am)	-202.9 ^a	Elgawhary and Lindsay (1972)
SO ₄ ²⁻	-177.97	Wagman et al. (1968)
UO ₂ ²⁺	-227.7	Fuger and Oetting (1976)

^aCalculated from given reference and other data in this table^bCalculated by Krupka and Jenne (1982)

where X, Y, Z represent different species and a, b, c represent coefficients of species.

$$\Delta G_{r,298}^0 = \sum \Delta G_f^0 \text{ products} - \sum \Delta G_f^0 \text{ reactants} \quad (2-2)$$

where ΔG_r^0 is the standard free energy change of the reaction.

$$\ln K^0 = [-\Delta G_r^0]/[RT] \quad (2-3)$$

where R is the gas constant (0.001987 Kcal/deg per mole) and T is the absolute temperature, and at 25°C (T = 298.15 K) $\log K^0 = (-\Delta G_r^0)/1.364$

Where values of equilibrium constants (K^C) were available at ionic strengths (μ) other than zero, equilibrium constant values at zero ionic strength (K^0) were calculated (Eq. 2-4) using the activity coefficients (γ_i) at 25°C calculated from the Davies (1962) equation (Eq. 2-5)

$$\log K^0 = \log K^C + [\sum \log \gamma \text{ products}] - [\sum \log \gamma \text{ reactants}] \quad (2-4)$$

$$\log \gamma_i = -0.509 Z_i^2 [\mu^{1/2}/(1 + \mu^{1/2}) - 0.3\mu] \quad (2-5)$$

where Z_i is the valence of the ion.

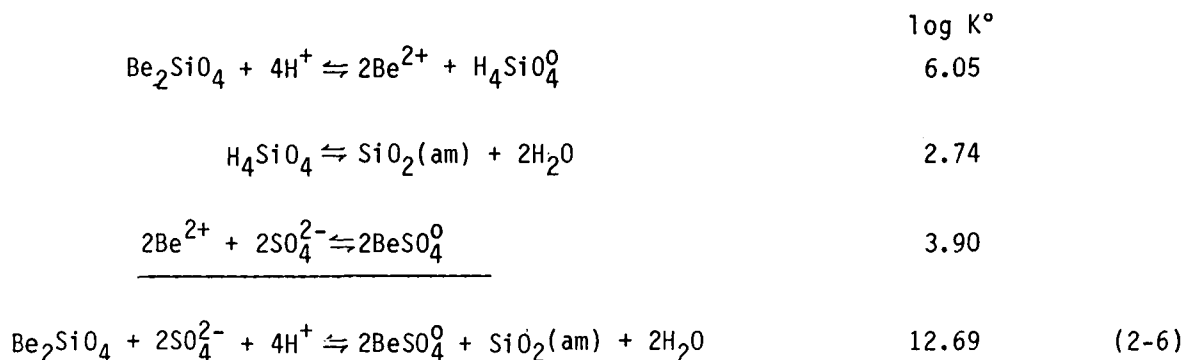
A preliminary set of equilibrium constants were selected from these compilations. However, it is difficult to determine whether the values are accurate from observation alone. Therefore, several subjective criteria were used to select appropriate constants. These criteria are listed below.

- Values (from sources such as Wagman et al. 1968, 1969, 1971; Parker et al. 1971; Smith and Martell 1976) were selected that recommend single values based on their recent reviews.
- In cases of differing multiple values for a reaction, the most recent values obtained with improved experimental techniques were chosen.
- Where possible, data for a sequence of solution species [e.g., five fluorinated species of vanadium (V), $VO_2F_n^{1-n}$ (n = 1 to 5)] were selected from a single source.

Based on the preliminary set of equilibrium constants, solid phase and solution species diagrams were developed to ascertain the nature of dominant aqueous species and potential solubility-controlling solids. For example, relative stability of solid phases and solution species of beryllium are reported in Figures 7-1 and 7-2. In the case of beryllium, hydroxo and fluoro complexes were the most important solution species (Figure 7-2). Therefore, an attempt was made to review the literature for these complexes and the selected values were reported (see Appendix A Table A-5).

The equilibrium reactions (Appendix A and the thermodynamic data in the geochemical code MINTeq) were used to construct the final diagrams reported in this publication. The method of construction of solid phase and solution species diagrams such

as reported here have been discussed by Pourbaix (1966), Garrels and Christ (1965), Rai and Lindsay (1975), Kittrick (1977), and Lindsay (1979). For example, to determine the influence of Be^{2+} complexation by SO_4^{2-} on the solubility of phenakite (BeSiO_4) in equilibrium with $\text{SiO}_2(\text{am})$, different reactions (given in Table A-5 and based on data in Table 2-1) were combined in the following manner and the $\log (\text{BeSO}_4^0)$ (Eq. 2-7) then plotted as in Figure 7-2.



By setting the activity equal to one (by convention) for pure compounds [Be_2SiO_4 , H_2O , and $\text{SiO}_2(\text{am})$], the equilibrium constant (K°) for the reaction in Eq. (2.6) becomes:

$$K^\circ = (\text{BeSO}_4^0)^2 / (\text{SO}_4^{2-})^2 (\text{H}^+)^4$$

Taking logarithms of both sides and rearranging the equation results in Equation (2.7)

$$\log (\text{BeSO}_4^0) = 1/2 \log K^\circ + \log \text{SO}_4^{2-} - 2\text{pH}$$

$$\text{and at } \log \text{SO}_4^{2-} = -3$$

$$\log (\text{BeSO}_4^0) = 3.37 - 2 \cdot \text{pH} \quad (2-7)$$

Other reactions were similarly plotted. For the solution species not reported in the figures, either adequate data were not available to calculate their activity or the species do not contribute significantly to the total concentration of element in solution. In these diagrams, the solution species that have the highest activities at a given pH are dominant. In the diagrams depicting relative solubility (e.g. Figure 7-1), the solid phases that maintain lowest activity are the most stable (in Figure 7-1 phenakite is the most stable solid).

Aqueous species were calculated under conditions anticipated in the utility waste environment. For most of the calculations, the assumed groundwater composition included $\text{SO}_4^{2-} = \text{Cl}^- = 10^{-3}\text{M}$, $\text{NO}_3^- = \text{F}^- = 10^{-4}\text{M}$, $\text{Br}^- = \text{I}^- = 10^{-5}\text{M}$, $\text{CO}_2 = 10^{-3.52}$, $\text{Na}^+ = \text{K}^+ = \text{Ca}^{2+} = 10^{-3}\text{M}$, and $\text{Mg}^{2+} = 10^{-4}\text{M}$ with a range in pH and E^H . Although the species calculations reported in the text (Sections 3 through 23) were made using the assumed groundwater composition, the thermodynamic data can be used to calculate speciation under other conditions as well.

Redox reactions in this report are written in terms of an electron activity so as to represent both chemical and electrochemical reactions by a single equilibrium constant. The negative logarithm of electron activity (pe) is related to the redox potential (E^H in volts) by $\text{pe} = 16.9 E^H$ (Lindsay 1979). Therefore, the maximum possible range in environmental redox potentials where water is stable is: pe values from 0 to 20.78 at pH = 0 or pe + pH values from 0 to 20.78.

Although the selected values for different solution complexes can be combined with the solubility reactions of solid phases (e.g., Figure 7-2) to determine the equilibrium concentrations in different environments, these calculations should only be used as a guide in cases where validation of these predictions have not yet been made. Precipitation/dissolution reactions in soils, especially for trace elements, have not been extensively studied. The available data vary in quality. Some studies identified solids and compared observed solubility products with the available thermodynamic data to determine the solubility-controlling solids. Other studies, where precipitation/dissolution was not the main objective, hypothesized the presence of solubility-controlling solids. However, because of the limited number of studies, all of the available literature was reviewed and critiqued on precipitation/dissolution attenuation mechanism.

ADSORPTION CONSTANTS

Adsorption is a widely recognized attenuation mechanism arising from the physico-chemical interaction of ionic solutes with the surfaces of mineral constituents or soil organic matter. This reaction reduces the mobility of the adsorbed solute relative to the migrating water front. Adsorption may be specific or nonspecific. Specific adsorption occurs when the solute interacts directly with the adsorbent surface in the inner Helmholtz plane. Nonspecific adsorption occurs through physical interaction of the solute with the adsorbent (e.g., Van der Waals forces) or through electrostatic retention as a counter ion in the diffuse double layer. Data pertaining to both specific and nonspecific adsorption were reviewed. To ensure that the compiled information was applicable to actual utility waste sites in

different geologic terrains, investigations from a number of sources were included, which evaluated adsorption/desorption of inorganic waste constituents on surface soils, subsoil, geologic materials, and model adsorbents (e.g., single minerals). Adsorption from utility waste leachate, possibly in contact with subsurface materials for long periods of time, may differ appreciably from short-term adsorption studies in inert electrolytes. Hence, the review also considered adsorption/desorption kinetics and the effects of solution characteristics (e.g., solution/solute matrix, competing and complexing ions) on adsorption, so that the adsorptive behavior of contaminants in the leachate could be clearly defined.

Based on a computerized search and literature review, the general content of each publication was summarized in tabular form according to attenuation constants, solid and solution phase characteristics, and experimental variables and procedures. This tabular summary was then used to judge the merit of the compiled literature. Evaluation criteria were designed to ensure that the tabulated attenuation data were experimentally defensible and acceptable for modeling purposes. The criteria were directed at the degree of adsorbent characterization, degree of solution characterization, and the adequacy of experimental procedures (Table 2-2). These criteria were applied in various degrees of severity depending on the amount of available literature. For example, criteria were mainly applied to elements where large amounts of data exist (e.g., Cu, Cd). For those elements where information was sparse, criteria were applied subjectively to eliminate data that were totally unacceptable. In some cases, data which did not pass the evaluation criteria were used to qualitatively assess element behavior and are cited in the written element review. All articles, publications, or reports passing the evaluation criteria were considered defensible and their data tabulated (Sections 3 through 23).

The compilation of attenuation constants derived from the critical review quantitatively describe the adsorption of utility waste constituents on specific soil and subsoil materials and mineral constituents. The tabulated information (Sections 3 through 23) represents an attenuation data base, which may be useful to qualitatively assess constituent migration in specific utility sites having similar geochemical/mineralogic characteristics. The attenuation data base, however, does not allow for quantitative prediction of constituent migration rates based solely upon knowledge of site subsurface mineralogy, chemistry, and leachate characteristics.

Many techniques are used for analyzing adsorption data, calculating descriptive constants, and modeling adsorption behavior. The most common adsorption models

Table 2-2

ADSORPTION/DESORPTION EVALUATION CRITERIA

<u>Evaluation Item</u>	<u>Criteria</u>
Adsorbent	Mineralogical characterization of soil or single adsorbent Surface area ^a Particle size ^a
Solution Phase	Equilibrium pH and Eh (soil pH and Eh accepted) Composition of solution phase
Experimental procedures	Adsorbate concentration below solubility levels Temperature Separated solution phase by filtration or high speed centrifugation

^aNot required, but helpful

are: 1) distribution coefficients, 2) Langmuir isotherms, 3) Freundlich isotherms, 4) BET isotherms, and 5) surface complexation. The mathematical formulation of these are described below. The nomenclature used below applies to the discussion of each element as well as the constants tabulated in the text (Sections 3 through 23).

Distribution Coefficient

The distribution coefficient, K_d , is defined as the ratio of the quantity of the adsorbate adsorbed per gram of solid to the amount of the adsorbate remaining in solution at equilibrium. The mass action expression ($K_d = \bar{S}/C$) is the common definition of the K_d in terms of the reaction $\bar{S} + C \rightleftharpoons S$, where \bar{S} = the free or unoccupied surface adsorption sites, C = the total dissolved adsorbate remaining in solution at equilibrium, and S = adsorbate on the solid at equilibrium. Describing the K_d in terms of this simple reaction assumes that \bar{S} is in great excess with respect to C and that $\bar{S} = 1$. However, K_d is not an isotherm but rather a single constant. It is valid only for the particular adsorbent used and applies only to those aqueous chemical conditions (e.g., adsorbate concentration, solution/electrolyte matrix) and the temperature under which it was measured.

Langmuir Isotherm

The Langmuir isotherm is described by:

$$S = \frac{K_L A_m C}{1 + K_L C} \quad (2-8)$$

where

S = moles adsorbed at equilibrium per gram of solid

A_m = the maximum adsorption capacity of the solid

K_L = the Langmuir adsorption constant which can be related to the binding energy of the adsorbate (magnitude is specific for units of C)

C = total adsorbate concentration in solution at equilibrium. (moles/L)

The above expression combines a mass action expression for the adsorption reaction $C + \bar{S} \rightleftharpoons S$, and a mass balance equation for surface sites, $A_m = \bar{S} + S$, where \bar{S} represents unoccupied surface sites. This expression assumes a finite number of surface sites (i.e., imposition of a mass balance on surface sites), which distinguishes the Langmuir equation from the K_d and the Freundlich equation (see below). Further, the Langmuir isotherm assumes that: 1) adsorption occurs on specific sites with no electrostatic or chemical interactions between adsorbate ions; 2) all adsorption sites are equivalent (i.e., for a given adsorbate the binding energy for all surface sites is the same); 3) the ability of an adsorbate ion to bind to a surface site is independent of whether or not the neighboring sites are occupied [i.e., the binding energy is independent of the adsorption density (S)] and 4) maximum adsorption is limited to mono-layer coverage of the surface sites, that is, adsorption does not occur on the new surface layer formed by the adsorbate.

By rearranging Eq. (2-8) as described below, a plot of C/S versus C results in a linear representation of adsorption data with a slope of $1/A_m$ and an intercept of $1/K_L A_m$.

$$C/S = 1/K_L A_m + C/A_m \quad (2-9)$$

Greater accuracy is obtained in estimating the slope of the curve than in estimating the intercept for reasonably low adsorbate concentrations used in most adsorption

experiments. Thus, a more accurate estimate of A_m can be obtained from adsorption data using Eq. (2-9) than other possible linearizations of Eq. (2-8) for which the intercept is equal to A_m or $1/A_m$.

In many cases, adsorption data in soils deviate from the single-site Langmuir Eqs. (2-8) or (2-9) above. Phosphate adsorption is an example of this. To describe these data, it has been postulated that either several energetically distinct sites are present and that adsorption onto each of these sites is of type 'i' following the Langmuir equation, or that two distinct mechanisms of adsorption occur on a single set of sites.

For adsorbate/adsorbent combinations where multiple surface sites may be responsible for adsorption, the Langmuir equation can be generalized as follows:

$$S = \sum \frac{(K_{L,i})(A_{m,i}C)}{1 + (K_{L,i})C} \quad (2-10)$$

The summation is over all possible sites 'i', where $A_{m,i}$ is the maximum quantity of the adsorbate on sites of type 'i', and $K_{L,i}$ is a constant which may be related to the binding energy for adsorbent site of type 'i'. In the two-site case, the total adsorption can be treated as the sum of a high energy and a low energy component and a plot of C/S versus C would consist of two straight line segments with different slopes.

When several adsorbates (e.g., Cd^{2+} , Zn^{2+} , HSeO_3^- , and AsO_3^{2-}) are present together in solution, strongly binding species will compete for available surface sites. This type of interaction always reduces the tendency for each individual ion to adsorb. If the system obeys the Langmuir isotherm, adsorption of an ion 'j' in the noncompetitive and competitive systems is given by:

$$S_j = \frac{(A_{m,j})(K_j)(C_j)}{1 + K_j C_j + \sum_i n_i K_i C_i} \quad (2-11)$$

where

S_j = adsorption density of 'j'

$A_{m,j}$ = maximum adsorption density of component 'j'

K_i and K_j = Langmuir binding constants for component 'i' and 'j'

C_i and C_j = equilibrium concentrations of component 'i' and 'j' in solution

$$n_i = A_{m,j}/A_{m,i}$$

The summation includes all competing adsorbates in the system. The factor 'n' corrects for those adsorbates that may take up more space or occupy more sites than others. Since $n = 1$ for competing species of similar size, n is rarely included in the above equation. However, it may be important when species of differing size compete for the same sites.

Freundlich Isotherm

Literature on non-Langmuirian adsorption behavior suggests that: 1) a nonuniformity exists among the adsorption sites; and 2) the change in the free energy of adsorption (ΔG_{ads}) becomes less negative as the adsorption density (S) increases, suggesting that the initial sites occupied are energetically the most favorable sites. Indeed at higher S, complexation of adsorbate ions with surface sites is not strictly analogous to complexation with dissolved ligands.

The Freundlich equation can be derived by assuming that the sites of a given energy in the interval $\Delta G_{ads} = d\Delta G_{ads}$ are Langmuirian and that the probability that a site has an adsorption energy in the interval $\Delta G_{ads} = d\Delta G_{ads}$ is exponential. However, no physical basis exists for assuming this exponential probability distribution. The isotherm can be written as:

$$S = K_F C^{1/n} \quad (2-12)$$

where K_F and n are constants, and n is typically greater than or equal to 1. For dilute solutions $n = 1$, but as the adsorption density increases, $n > 1$. The range of S for which $n = 1$ and the value of S for which n begins to increase differs according to the specific adsorbate/adsorbent pair (Benjamin and Leckie 1981). In contrast to the Langmuir-type isotherm, the thermodynamic interpretation of the Freundlich isotherm in Eq. (2-12) is that the adsorption energy varies with $\ln(S)$. This energy dependence is not unique, however, since it depends upon the assumed probability distribution.

It should be noted emphatically that the empirical observation that a given set of adsorption data can be fitted to a Langmuir or a Freundlich equation does not necessarily establish a constant or logarithmic dependence of adsorption on

adsorption density S . A fit to the Freundlich equation, however, may be interpreted as evidence for inhomogeneity among surface adsorption sites, or possibly surface interaction between adsorbed species.

BET Isotherm

The BET isotherm describes multi-layer Langmuirian adsorption (Brunauer et al. 1938). Multi-layer adsorption typically results from physical or van der Waals bonding of gases or vapors to solids. The BET isotherm has also been applied to adsorption from soil solution. The adsorption of molecules to the surface of particles forms a new surface layer to which additional molecules adsorb. If it is assumed that the energy of adsorption on all successive layers is equal, the BET equation is,

$$S = \frac{K_B A_m C}{(C_s - C) \{1 + (K_B - 1) (C/C_s)\}} \quad (2-13)$$

where A_m = the maximum adsorption density of the first layer, K_B = a constant related to the adsorption energy, and C_s = the concentration of the adsorbate at saturation. The BET equation reduces to the Langmuir equation if $K_B \gg 1$ and $C/C_s \ll 1$. The BET isotherm differs from the Freundlich and Langmuir isotherms in the assumed location of the sites and the creation of new sites with the occupation of each existing site. The BET equation has received extensive application for the determination of the surface area of solids from gas adsorption data.

Surface Complexation Models

Surface complexation models describe adsorption in a more detailed fashion than adsorption isotherms. The surface is treated as an array of hydroxyl groups designated as XOH , where X represents structural Si, Fe, Ti, Al, Mn or other atoms at the solid-liquid interface (Figure 2-1). These hydroxyl groups or adsorption "sites" can be treated as ligands which: 1) have specific acid/base characteristics, and 2) form complexes with electrolyte or metal ions or other ion pairs in solution. The same set of assumptions made above for the Langmuir isotherm are assumed to apply to surface complexation models. Adsorption reactions (i.e., the coordination of these solute ions with surface hydroxyl groups) are treated by analogy with complexation in bulk solution. Thus, for an assumed stoichiometry of reaction, an association (adsorption) constant can be used to describe the adsorption reaction.

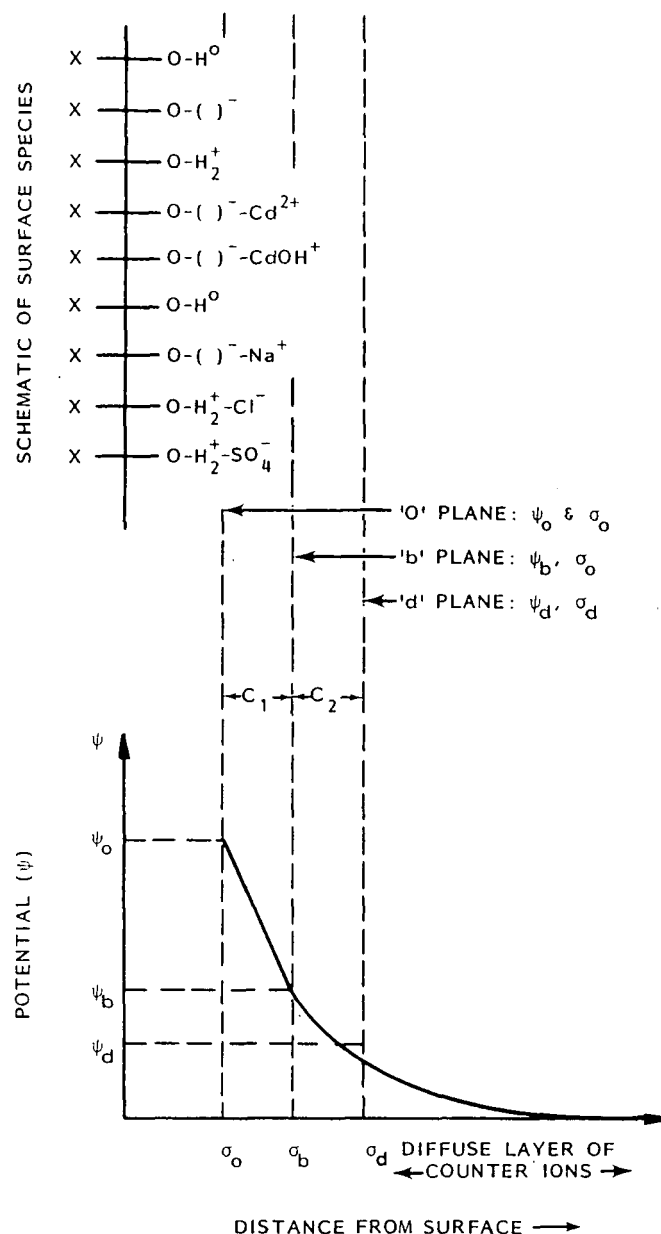


Figure 2-1. Schematic representation of charge distribution and adsorbed species

A fundamental difference between adsorption reactions at the solid-solution interface and aqueous coordination reactions in bulk solution, is that a variable electrostatic interaction energy exists between the charged adsorbing ion and the surface charge on the solid (Figure 2-1). A difference in chemical potential of the charged ion develops near the surface due to the electrostatic potential, ψ , produced by the surface charge, σ . Because of these nonideal interactions, the activities of ions approaching the surface are modified by the energy required to

bring them from the bulk solution to a specific adsorption plane within the electric double layer. The ion activities near the surface $[(\text{Ion})_s]$ are related to the activities in bulk solution $[(\text{Ion})_{\text{bulk}}]$ by the following equation:

$$(\text{Ion})_s = (\text{Ion})_{\text{bulk}} [\exp(-ZF\psi/RT)] \quad (2-14)$$

where Z is the positive or negative charge of the ion, F is the Faraday constant, R is the gas constant, T is temperature in Kelvin, and ψ is the electrostatic potential on the surface or at the designated adsorption plane within the double layer. Westall and Hohl (1980) have described several surface complexation models (constant capacitance, VSC-VSP, and triple layer) and their relation to one another. The major differences between these models are: 1) the set of surface species considered (e.g., whether surface-electrolyte species are considered); and 2) the description of the electric double layer (i.e., the definition and assignment of ions to "mean" planes of adsorption within the double layer as in Figure 2-1).

As an example, the relevant constants for the triple layer model will be defined for the case where adsorption occurs from a solution containing NaCl as the major electrolyte and Cd^{2+} and SO_4^{2-} ions as the dilute adsorbates. Surface ligands consist of a single amphoteric surface site, XOH . The triple layer model treats the solid-solution interface as being composed of two constant capacitance layers bounded by a diffuse layer (Figure 2-1). Specifically adsorbed H^+ and OH^- ions are located in the surface 'o' plane and contribute to the surface charge σ_o , and experience an electrostatic potential, ψ_o . Electrolyte ions and dilute adsorbate ions are located in the 'b' or inner Helmholtz plane and are bound pairwise to oppositely charged surface sites by both a specific chemical and an electrostatic energy. These ions contribute to the charge, σ_b , and are subject to an electrostatic potential, ψ_b . The outer Helmholtz plane or the 'd' plane is the inner boundary of the diffuse region of nonspecifically bound counterions. Regions of constant capacitance, C_1 and C_2 , separate the 'o' and 'b' planes and the 'b' and 'd' planes, respectively.

The surface hydrolysis and complexation reactions and the associated intrinsic equilibrium constants for the surface species shown in Figure 2-1 are given in Table 2-3. The subscript 's' used on ions (e.g., H_s^+ , in the reactions in Table 2-3) represents an ion in the electric double layer rather than in bulk solution and is explicitly defined by Eq. (2-14). The complexation reactions are written in terms of deprotonated and protonated surface sites. K_{a1}^{int} and K_{a2}^{int} are the first and second surface acidity constants and the other K_x^{int} are the intrinsic adsorption

Table 2-3

TRIPLE LAYER MODEL REACTIONS AND INTRINSIC
EQUILIBIRUM CONSTANTS FOR SURFACE SPECIES SHOWN IN FIGURE 2-1

Reactions*	Intrinsic Constants†
Surface Hydrolysis	
$XOH_2^+ \rightleftharpoons XOH + H_S^+$	K_{a1}^{int}
$XOH \rightleftharpoons XO^- + H_S^+$	K_{a2}^{int}
Cation Complexation	
$XO^- + Na_S^+ \rightleftharpoons (XO^- Na^+)^0$	K_{Na}^{int}
$XO^- + Cd_S^{2+} \rightleftharpoons (XO^- Cd^{2+})^+$	K_{Cd}^{int}
$XO^- + Cd_S^{2+} + H_2O \rightleftharpoons (XO^0 CdOH^+)^0 + H_S^+$	K_{CdOH}^{int}
Anion Complexation	
$XOH_2^+ + Cl_S^- \rightleftharpoons (XOH_2^+ Cl^-)^0$	K_{Cl}^{int}
$XOH_2^+ + (SO_4^{2-})_S \rightleftharpoons (XOH_2^+ SO_4^{2-})^-$	$K_{SO_4}^{int}$

*The activity of surface species (species with subscript s) are related to the activities of these species in bulk solution by Equation (2-14). H_S^+ species exist at plane o that has potential ψ_o , while all others exist at plane b that has potential ψ_b (Figure 2-1).

†Relationship of K^{int} to the products and reactants is shown through the following example

$$K_{Na}^{int} = \frac{(XO^- Na^+)^0}{(Na_S^+)(XO^-)} = \frac{(XO^- Na^+)^0}{(XO^-)(Na^+)[\exp(-F\psi_b/RT)]}$$

$$= K_{Na} [\exp(F\psi_b/RT)]$$

constants for cation or anion "X". The exponential term is the Boltzman factor, Eq. (2-14), and accounts for electrostatic and activity effects. The K_x are the mass action expressions for individual reactions, e.g.,

$$K_{a1} = \frac{[XOH](H^+)}{[XOH_2^+]} \quad \text{or,} \quad K_{CdOH} = \frac{[XO^-CdOH^+](H^+)}{[XO^-](Cd^{2+})} \quad (2-15)$$

Activity coefficients for surface species are, by convention, set equal to one. Thus [] represents the concentration of surface species XOH , XO^- , and XOH_2^+ in mole per liter, and () represents the activity of an ion in the bulk solution.

A particular set of surface species (Figure 2-1) is justified when predictions based on these equations describe the experimental data (e.g., the pH adsorption edge). It should be noted that the selection of surface species and hence the stoichiometry of complexation reactions which describe the data, depend upon which model of the electrical double layer is used.

The triple layer model, which has been described above, consists of: 1) the set of reactions describing complexation of solution species (electrolyte and adsorbate) with the surface; 2) a surface-site mass-balance equation for $[XOH]_{tot}$; and 3) surface-charge balance equations. This set of simultaneous equations is iteratively solved to obtain a self-consistent set of surface and solution species. For this example the quantity of Cd adsorbed, S_{Cd} , is calculated by summing the concentrations of the Cd surface species,

$$S_{Cd} = ([XO^-Cd^{2+}] + [XO^-CdOH^+])/M \quad (2-16)$$

where M is the grams of solid per liter of solution.

In summary, the triple layer model requires a set of constants to define the interactions of electrolyte and adsorbate ions with amphoteric surface hydroxyl sites: K_{a1}^{int} , K_{a2}^{int} , K_{Na}^{int} , K_{Cl}^{int} , K_{Cd}^{int} , K_{CdOH}^{int} , $K_{SO_4}^{int}$, and capacitances C1 and C2 as parameters characterizing the properties of the electric double layer. In addition, measurements are needed of the specific surface area, $S(m^2/g)$, and the surface hydroxyl site density, $N_s(\text{sites}/nm^2)$, of the solid. Although the triple layer model requires more constants than isotherm equations, these constants, unlike those parameterizing isotherm equations, apply over a range of electrolyte concentrations (10^{-4} to 1 M), pH (4 to 10) and dilute adsorbate (e.g., Cd) concentrations.

A limitation of the triple layer model and surface complexation models as presently formulated is their assumption of Langmuirian adsorption behavior. Experimentally all surface sites are not energetically equal and ΔG_{ads} is dependent on S . As a direct consequence of the Langmuirian assumption, the intrinsic constants are observed to decrease in value when the surface adsorption density, S , exceeds a critical value S_{CR} . This critical value, S_{CR} , depends upon the combination of adsorbate and adsorbent (Benjamin and Leckie 1981). The functional dependence of K^{int} on S can be experimentally determined and incorporated into the triple layer model description of adsorption. Finally, it should be stated that surface complexation models and in particular the triple layer model can be easily generalized to describe multiple surface sites, SOH, TOH, etc., by including an appropriate set of reactions describing the complexation of these sites with solution species.

USE OF ATTENUATION CONSTANTS TO PREDICT PORE WATER CONCENTRATIONS - AN EXAMPLE

A simple example is discussed below to illustrate the use of attenuation constants and their importance in reducing the mobility of solute in utility waste leachate. In this example, 538 liters (L) of acidic utility waste leachate containing 10^{-6} moles per liter (M) Cd^{2+} is assumed to infiltrate into and saturate one cubic meter of subsoil. The leachate and subsoil characteristics along with other assumptions are given in Fig. 2-2. Sample calculation will then predict the solution concentration of Cd^{2+} in the pore waters after the leachate has equilibrated with the subsoil material. Both adsorption and precipitation reactions will be considered.

Adsorption Reactions Alone

In this example we assume that the leachate instantaneously equilibrates with the subsoil and that the Cd^{2+} adsorption follows Langmuirian behavior. The mathematical derivation of the Langmuir isotherm assumes that a fixed concentration of adsorption sites exist (S_T), which defines a maximum adsorption capacity (A_m). The adsorption reaction may be written in a fashion analogous to a solution complexation reaction, i.e.,



where \overline{S}_s is unoccupied surface adsorption sites, Cd^{2+} the solution activity of cadmium, and \overline{SCd} the adsorption sites occupied by Cd. An equilibrium constant for Eq. (2-17) is defined in Eq. (2-18).

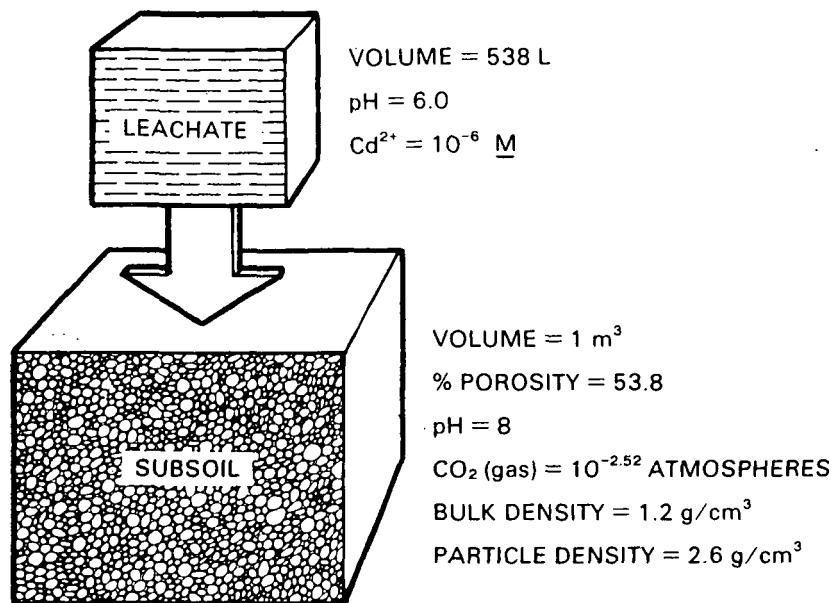


Figure 2-2. Schematic showing characteristics of leachate and subsoil. Additional assumptions include: activity coefficient of one, no complexation, no competing ion effects, adsorption constant values ($K_L = 0.631 \text{ L}/\mu\text{M}$, $A_m = 2.6 \mu\text{M/g}$) and precipitation/dissolution constant value ($\text{CdCO}_3 + 2\text{H}^+ \rightleftharpoons \text{Cd}^{2+} + \text{CO}_2(\text{g}) + \text{H}_2\text{O}$ $\log K = 4.41$) taken from Singh (1979) (Table 9-1) and Ball et al. (1980), respectively.

$$K = \frac{(\overline{\text{SCd}})}{(\overline{S_s}) (\text{Cd}^{2+})} \quad (2-1)$$

Taking the difference between the total sites (S_T) and the occupied sites gives the unoccupied surface adsorption sites (Eq. 2-19).

$$\overline{S_s} = S_T - \overline{\text{SCd}} \quad (2-1)$$

Substituting Eq. (2-19) in Eq. (2-18) and solving for $\overline{\text{SCd}}$ leads to Eq. (2-20)

$$\overline{\text{SCd}} = \frac{K S_T (\text{Cd}^{2+})}{1 + K (\text{Cd}^{2+})} \quad (2-2)$$

Equation (2-20) is the common form of the Langmuir equation where K is the Langmuir adsorption constant (K_L) and S_T is the Langmuir adsorption maximum (A_m).

Calculating the aqueous Cd concentration in equilibrium with subsoil using the Langmuir Eq. (2-20) requires solution of a mass balance equation:

$$C_T = C_S + C_{Ads} - C_L \quad (2-21)$$

where C_T is total moles of Cd added to the subsoil as a leachate, C_S is total moles of Cd in solution at equilibrium, C_{Ads} is total moles of Cd adsorbed by subsoil, and C_L is moles of Cd lost from the subsoil through water mass flow (water flow is assumed not to occur from the subsoil in this example, thus $C_L = 0$).

Equation (2-21) can now be expressed on a concentration basis:

$$C_0 V_1 = C_e V_2 + \overline{SCd} W \quad (2-22)$$

where C_0 is the initial leachate concentration in μM , V_1 is the volume of leachate in liters, C_e is the equilibrium solution concentration of Cd^{2+} in μM , V_2 is the volume of total pore water in the subsoil in liters, \overline{SCd} is the adsorbed Cd concentration in $\mu M/g$, and W is dry mass of the subsoil in grams (g). The Langmuir Eq. (2-20) can now be substituted for \overline{SCd} in Eq. (2-22) which yields

$$C_0 V_1 = C_e V_2 + W \frac{K A_m C_e}{1 + K C_e} \quad (2-23)$$

All the parameters in Eq. (2-23) except C_e are known (Fig. 2-2). This equation can be rearranged into a polynomial (Eq. 2-24) and solved for C_e , the equilibrium concentration of C_d (μM) in pore water.

$$C_e^2 K V_2 + C_e (W K A_m - C_0 V_1 K + V_2) - C_0 V_1 = 0 \quad (2-24)$$

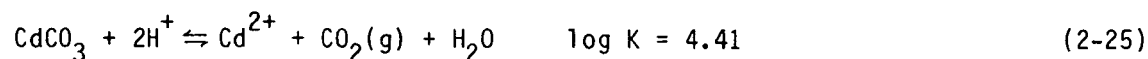
The predicted equilibrium Cd concentration thus calculated was found to be $2.74 \times 10^{-4} \mu M$ or $2.74 \times 10^{-10} M$. Chemical attenuation through adsorption alone, therefore, reduced the Cd concentration from $10^{-6} M$ to $2.74 \times 10^{-10} M$.

Resubstituting this value of C_e back into Eq. (2-20) allows calculation of the percent saturation of the adsorption sites (\overline{SCd}/A_m), which in this case is extremely low (0.017%). Thus, the subsoil will continue strong adsorption of Cd until an adsorption density of 50% has been attained.

The subsoil used in this example had a fairly high A_m and K_L . If the A_m and K_L of this subsoil were lower, the predicted Cd concentration would proportionally be higher.

Precipitation Alone

When considering only precipitation, we assume that octavite (CdCO_3) precipitated as a result of an increase in pH of the leachate from 6.0 to 8.0 due to its interaction with subsoil. Using the precipitation/dissolution reaction of CdCO_3 Eq. (2-25), which may be termed an attenuation, we can calculate the maximum equilibrium concentration of Cd^{2+} that will be present in subsoil pore water.



$$K = \frac{(\text{Cd}^{2+}) (\text{CO}_2(\text{g}))}{(\text{H}^+)^2} \quad (2-26)$$

Field observations indicate that the CO_2 pressure in soil and subsoil pore space is enriched relative to atmospheric concentrations. Therefore, for the purpose of this example CO_2 concentrations 10 times higher than that of the atmosphere were used. Using the given subsoil values (Fig. 2-2) of H^+ , $\text{CO}_2(\text{g})$, and K , the equilibrium Cd^{2+} activity was calculated from Eq. (2-26) and was found to be $10^{-9.07}$ M.

Combination of Precipitation and Adsorption

Assuming precipitation kinetics are rapid and that CdCO_3 precipitation occurs in a top few cm of subsoil, the Cd^{2+} concentration in the pore water of the rest of the subsoil can be calculated from Eq. (2-24) using the adsorption constants and other values given in Figure 2-2. Additionally, it is assumed that the subsoil (below the few top cm) is saturated with water with initial concentration of $10^{-9.07}$ M Cd^{2+} (see 'Precipitation Alone' above). Solving Eq. (2-24) yields a predicted equilibrium concentration (C_e) of 2.32×10^{-7} μM or 2.32×10^{-13} M. Thus, the combined effects of precipitation and adsorption markedly reduced or attenuated the concentration of Cd^{2+} in the leachate from 10^{-6} M to 2.32×10^{-13} M.

General Conclusions

The example calculations illustrate the use of selected attenuation constants (solubility products, Langmuir adsorption constants) in calculation of subsurface attenuation. Clearly, the calculations are simplified. However, they do illustrate the use and importance of the information which is reviewed and compiled in this report. The initial Cd^{2+} concentration (10^{-6} M) of leachate used in the above example was approximately 11 times higher than proposed (Environmental Protection

Agency 1980) drinking water concentration limit ($10^{-7.06}$ M). Consideration of adsorption or precipitation alone, or the combination of both mechanisms reduced Cd^{2+} concentration in pore water to several orders of magnitude below the drinking water limit. The predicted concentrations in the subsoil have little quantitative value but do show the potentially large attenuation capacity of some subsoils. As described in detail in the report, subsoils of differing chemical and mineralogic content vary appreciably in their attenuation capacity. Attenuation is also dependent upon the chemical form (e.g., cationic, anionic) of the utility waste constituents. Additionally, chemical interaction with other solutes present in leachate or ground water (e.g., complexation) serves to increase the solubility of solid phases and reduce adsorption. These and other attenuation factors must be considered to accurately estimate element mobility. Chemical attenuation processes need to be combined with hydrologic transport processes to predict solution concentration as a function of time and location in subsurface environments. This combination requires the use of geohydrochemical codes. EPRI is currently funding research efforts to develop such codes along with the necessary data bases.

Section 3

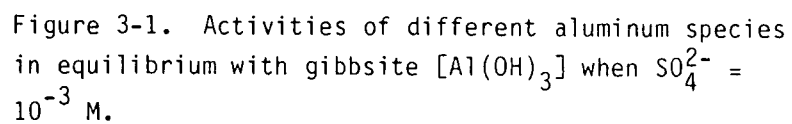
ALUMINUM

Aluminum (Al) exhibits complex and varied geochemical behavior in soils, subsoils and ground water. Certain anions (e.g., SO_4^{2-} , F^-) form strong aqueous complexes with Al which may dominate solution speciation at higher ligand concentrations. Al hydrolyzes readily at pH values >5 . The activity of Al^{3+} in soil and ground waters is controlled primarily by precipitation/dissolution reactions. Gibbsite [$\text{Al}(\text{OH})_3(\text{c})$] appears as a common crystalline solubility control in many geochemical environments, while alunite and basaluminite are important at lower pH and higher SO_4^{2-} concentrations. Ion exchange is an important retention mechanism in acid-to-neutral pH regimes. The buildup of exchangeable Al leads to soil acidity. Exchangeable Al on layer lattice silicates may hydrolyze, creating stable interlayer polymers that reduce cation exchange capacity. Aluminum competes strongly for cation exchange sites with Ca and other cations.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIES

Aluminum exhibits only a +3 valence state in its compounds and solutions. In addition to oxides and hydroxides, aluminum forms aluminosilicates. In SO_4^{2-} rich environments, it forms sulfate minerals such as alunite [$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$] and basaluminite [$\text{Al}_4(\text{OH})_{10}\text{SO}_4 \cdot 5\text{H}_2\text{O}$]. $\text{Al}(\text{OH})_3(\text{am})$ has fast precipitation kinetics and is the most soluble form of aluminum hydroxide (Lindsay 1979). $\text{Al}(\text{OH})_3(\text{am})$ slowly transforms to crystalline forms that have lower solubility. Most of the aluminosilicate clays such as kaolinite and montmorillonite are more stable than the crystalline aluminum hydroxides (Lindsay 1979).

Because gibbsite is one of the most stable hydroxides and is identified in many soils and sediments, it is generally used to estimate Al^{3+} activities. Thus, to determine the relative abundance of Al^{3+} species in ground waters representative of leachates, activities of different Al^{3+} species in equilibrium with gibbsite were plotted (Figure 3-1) using the thermodynamic data (Ball et al. 1980) contained in the geochemical model MINTEQ (Felmy et al. 1983). Under the assumed conditions (Figure 3-1), sulfate makes strong complexes with Al^{3+} such that the predominant aqueous species of Al at pH values <5 are Al^{3+} and AlSO_4^+ . Although the F^- complexes



PRECIPITATION/DISSOLUTION

3-2

and Brydon 1969). Hsu (1977) states that among the three polymorphs of aluminum hydroxides, only gibbsite is common in soils and bauxite.* Among the ten soil classification orders, gibbsite has been reported to be a major mineral in oxisols and some inceptisols; it is a common, but a minor component in ultisols (Hsu 1977). Whether gibbsite or aluminosilicate clays control Al activities in soils depends on the weathering environment.

ADSORPTION/DESORPTION

The adsorption of Al by soils and soil clays has been the subject of considerable study in the agronomic literature because of its importance in soil acidity and Al toxicity in acid soils. Aluminum exhibits complex solution chemistry, with hydrolysis and polymerization occurring at pH values in excess of 5 (Figure 3-1, Chakravarti and Talibudeen 1961, Richburg and Adams 1970). The hydrolysis behavior of Al strongly influences the adsorption chemistry. To a large extent, Al adsorption is governed by complexation with organic matter (Kerndorff and Schnitzer 1980; Wada and Gunjigake 1979) or exchange on soil clays (e.g., Coulter 1969a); however, limited specific adsorption by hydrous oxides or amorphous aluminosilicates may occur below pH 5 (Table 3-1).

The main constituent of soil acidity appears to be exchangeable and nonexchangeable Al on soil cation exchange sites, principally those associated with layer lattice silicates (Coulter 1969b; Bache 1974; Jackson 1963; Coleman and Thomas 1967). Acidity is generated by surface hydrolysis and polymerization of adsorbed Al^{3+} or solution hydrolysis of Al^{3+} liberated by ion exchange (Bache 1974, Coleman and Thomas 1967). Accounts of intercalation of 2:1 phyllosilicates in acid soils by $\text{Al}(\text{OH})$ polymers are numerous (e.g., Rich 1960, 1968; Klages and White 1957). These nonexchangeable interlayer materials form from surface hydrolysis/condensation of exchangeable Al or adsorbed hydrolysis species. The resulting polymers reduce cation exchange by masking sites of permanent negative charge.

Cation exchange reactions of Al in soil are affected by solution pH, by distribution of exchangeable cations in solution and on the exchange surface, and by degree of Al solution hydrolysis. As measured by selectivity coefficients and Langmuir constants, Al is more strongly bound than Ca to cation exchange sites of layer lattice silicates and soil (McBride and Bloom 1977, Kozak and Huang 1971, Pleysier et al. 1979). In contrast, K may be selectively adsorbed over Al in soil (Pleysier et al.

*Hsu (1977) has done an excellent review on the occurrence of gibbsite and the hydroxides and oxyhydroxides in soils and sediments.

1979, Coulter 1969b). Hydrolyzed forms of Al compete effectively with K for exchange sites on montmorillonite but are hindered in vermiculite (Somasiri and Huang 1974). This phenomenon is related to the degree of expansibility of the clay mineral as well as to the charge and size of the Al-hydrous ions. As noted with other hydrolyzeable cationic metals (e.g., Cu, Pb, Zn), hydrolyzed species of Al are more readily adsorbed by Si than by the free ion (Al^{3+}) (Hahn and Stumm 1968).

Table 3-1. ADSORPTION CONSTANTS FOR ALUMINUM

Adsorbent			Adsorbate		Electrolyte			Adsorption Measurement		References
Identity ^(a)	CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants ^(b)	Value ^(c)		
Clay Minerals										
Montmorillonite,										
untreated	-	-	0 - 0.002	-	-	4.0	A _m , K _L	(660-720, 5.8-6.1)	McBride and Bloom 1977	
Ca-saturated	-	-	0 - 0.002	CaCl ₂	0.01	4.0	A _m , K _L	(890, 4.7)		
Na-saturated	-	-	0.01	KCl	0.03	3.6	A, K _K ^{Al}	320, 14	Somasiri and Huang 1974	
						4.0		480, 24		
						4.1		660, 42		
						4.2		800, 62		
						4.4		930, 150		
						5.4		960, 160		
Vermiculite										
Na-saturated	-	-	0.01	KCl	0.03	3.4	A, K _K ^{Al}	420, 10		
						4.0		600, 12		
						4.2		590, 7.2		
						4.4		650, 7.4		
						5.4		430, 1.5		
Silica	-	205	10 ^{-6.7} - 10 ^{5.4}	-	-	5.00	A _m , K _L	100, 4.6	Hahn and Stumm 1968	
						5.25		560, 4.8		
Soil	% Clay	% O.C.								
	10	5.6	-	-	-		K _{Ca} ^{Al}	330	Bache 1974	
	3	2.1	-	-	-		K _{Ca} ^{Al}	3900		
	13	3.1	-	-	-		K _{Ca} ^{Al}	250		
	11	0.3	-	-	-		K _{Ca} ^{Al}	1700		
	3	0.8	-	-	-		K _{Ca} ^{Al}	3900		
	8	5.3	-	-	-		K _{Ca} ^{Al}	86		
	24	1.1	-	-	-		K _{Ca} ^{Al}	120		

Table 3-1 (Contd). ADSORPTION CONSTANTS FOR ALUMINUM

Adsorbent					Adsorbate		Electrolyte			Adsorption Measurement		References
Identity (a)		CEC meq/100g	S ₂ A. m ² /g		Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)		
Soil	% Clay	% O.C.										
	19	1.0	-	-	-							
	10	0.4	-	-	-	CaCl ₂	0.01	-	K ^{Al} _{Ca}	350		
	2	0.9	-	-	-	CaCl ₂	0.01	-	K ^{Al} _{Ca}	2.7		
Peat	-	-	-	-	-	CaCl ₂	0.01	-	K ^{Al} _{Ca}	0.13		
						CaCl ₂	0.01	-	K ^{Al} _{Ca}	18		
Soil	Depth	% Clay	% O.C.				ΣCl ⁻	Soil				
	0-20 cm	14	1.11	3.26	-	10 ⁻³ - 10 ⁻⁵	KCl, CaCl ₂	0.01	4.80	ΔG ^{oK} _{Al} , ΔG ^{oCa} _{Al}	2.69, -2.04	Pleysier et al. 1979
	20-40	22	0.69	3.34	-	10 ⁻³ - 10 ⁻⁵	KCl, CaCl ₂	0.01	4.90	ΔG ^{oK} _{Al} , ΔG ^{oCa} _{Al}	2.15, -2.18	
	40-60	26	0.55	3.14	-	10 ⁻³ - 10 ⁻⁵	KCl, CaCl ₂	0.01	4.85	ΔG ^{oK} _{Al} , ΔG ^{oCa} _{Al}	2.01, -1.66	
	60-80	26	0.41	2.93	-	10 ⁻³ - 10 ⁻⁵	KCl, CaCl ₂	0.01	5.20	ΔG ^{oK} _{Al} , ΔG ^{oCa} _{Al}	2.03, -2.01	
	80-100	26	0.32	2.88	-	10 ⁻³ - 10 ⁻⁵	KCl, CaCl ₂	0.01	5.15	ΔG ^{oK} _{Al} , ΔG ^{oCa} _{Al}	2.09, -1.31	

(a) O.C. = organic carbon

(b) A_m = Langmuir adsorption maximum, μmol g⁻¹

K_L = Langmuir constant, log M⁻¹

A = adsorption, μmol g.

K_M^{Al} = selectivity coefficient

ΔG^{oM}_{Al} = free energy of exchange, kcal eq⁻¹

(c) () = estimated values

Section 4

ANTIMONY

Antimony (Sb) is a multivalent element with Sb(III) species $[\text{Sb}(\text{OH})_3^0]$ dominant under reducing conditions and Sb(V) species $[\text{Sb}(\text{OH})_6^-]$ dominant under oxidizing conditions. Antimony (V) forms several polynuclear species in aqueous solutions; these species contribute significantly to the total Sb only at high Sb concentrations ($>10^{-2}\text{M}$). All of the known Sb compounds are very soluble; therefore, Sb concentrations are not expected to be solubility limited. Very little is known about adsorption/desorption behavior of Sb. Because of its anionic character under oxidizing conditions, adsorption by hydrous oxides at low pH values may be significant.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIES

Antimony, a multivalent element, exhibits -3, 0, +3, and +5 valence states. Antimony (III) and (V) are the stable oxidation states in aqueous solutions. Most of the Sb(V) compounds are very soluble and Sb in nature primarily occurs as Sb_2S_3 or Sb_2O_3 (Baes and Mesmer 1976). Thermodynamic data (see Appendix A, Table A-1) were used to predict the geochemical behavior of Sb. Figure 4-1 illustrates the dominant aqueous species for the Sb-H₂O system. The Sb(V) species $[\text{Sb}(\text{OH})_6^-]$ is predominant in oxidizing environments ($\text{pe} + \text{pH} \geq 11.4$) and at pH values >2.8 . The Sb(III) species $[\text{Sb}(\text{OH})_3^0]$ is predominant in relatively reducing environments ($\text{pe} + \text{pH} \leq 11.4$) at pH values between 1.5 and 11.2.

The distribution of Sb aqueous species in equilibrium with Sb_2O_3 (cubic) is illustrated in Figure 4-2. As expected, $\text{Sb}(\text{OH})_3^0$ is the predominant hydrolysis species at low redox potentials with $\text{Sb}(\text{OH})_6^-$ becoming increasingly important at high redox potentials. The species $\text{Sb}_2\text{S}_4^{2-}$ will be important in reducing environments if the total sulfide concentration exceeds $10^{-6.0}\text{M}$. Figure 4-2 also shows that the concentration of Sb in equilibrium with Sb_2O_3 will be a function of pH and Eh and will always be equal to or greater than $10^{-4.2}\text{M}$.

Figures 4-3 and 4-4 show the distribution of Sb(V) species as a function of pH. The only known Sb(V) solid phase, $\text{Sb}_2\text{O}_5(\text{c})$, is highly soluble. Therefore, various total concentrations of Sb were examined. At 0.001M total Sb, $\text{Sb}(\text{OH})_5^0$ and $\text{Sb}(\text{OH})_6^-$ are

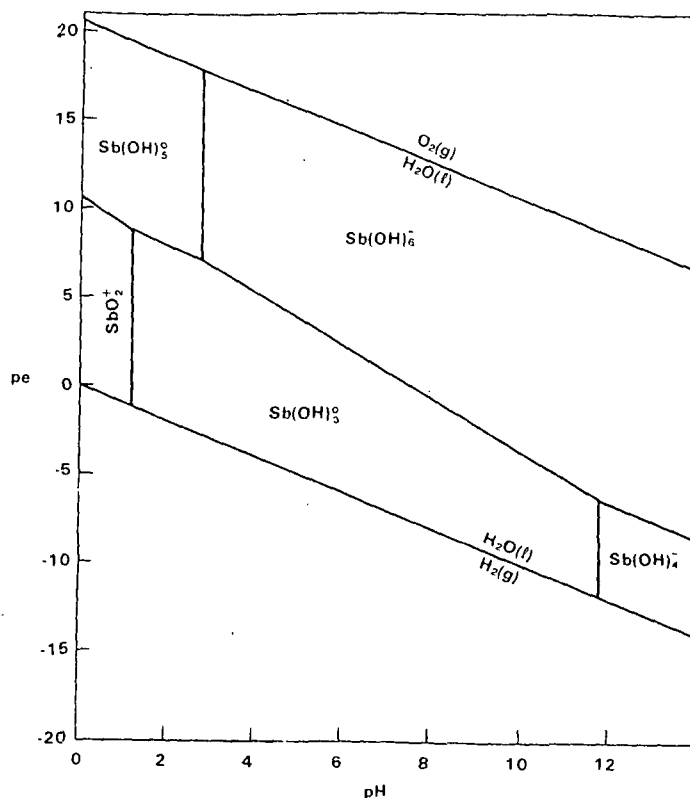


Figure 4-1. pe-pH diagram for Sb-H₂O system, at 25°C. The outlined regions indicate the conditions under which the given Sb solution species is predominant.

the dominant species with the polynuclear species $\text{Sb}_{12}(\text{OH})_{64}^{4-}$ and $\text{Sb}_{12}(\text{OH})_{65}^{5-}$ present in very small quantities. The Sb(III) species [$\text{Sb}(\text{OH})_3^0$, $\text{Sb}_2\text{S}_4^{2-}$, $\text{Sb}(\text{OH})_4^-$] will be unimportant except in reducing environments. As with all polynuclear complexes, the importance of the $\text{Sb}_{12}(\text{OH})_x$ species increases as the total Sb increases. In Figure 4-4, the $\text{Sb}_{12}(\text{OH})_{64}^{4-}$ species is dominant near pH 2 when total Sb is 0.01 M. It should be noted that at low pH, even though the concentration of $\text{Sb}(\text{OH})_3^0$ is slightly higher than $\text{Sb}_{12}(\text{OH})_{64}^{4-}$, the $\text{Sb}_{12}(\text{OH})_{64}^{4-}$ actually contains a far greater fraction of the total antimony because of the 12 Sb atoms per molecule of polynuclear complex.

Even though fairly high Sb concentrations were selected for Figures 4-3 and 4-4, the solubility products of known Sb solids are never exceeded. The Sb species under oxidizing environments and the environmental range of pH are negatively charged; therefore, one would expect Sb to be highly mobile in oxidized environments. The solubility of Sb as a function of redox is further illustrated in Figure 4-5 in

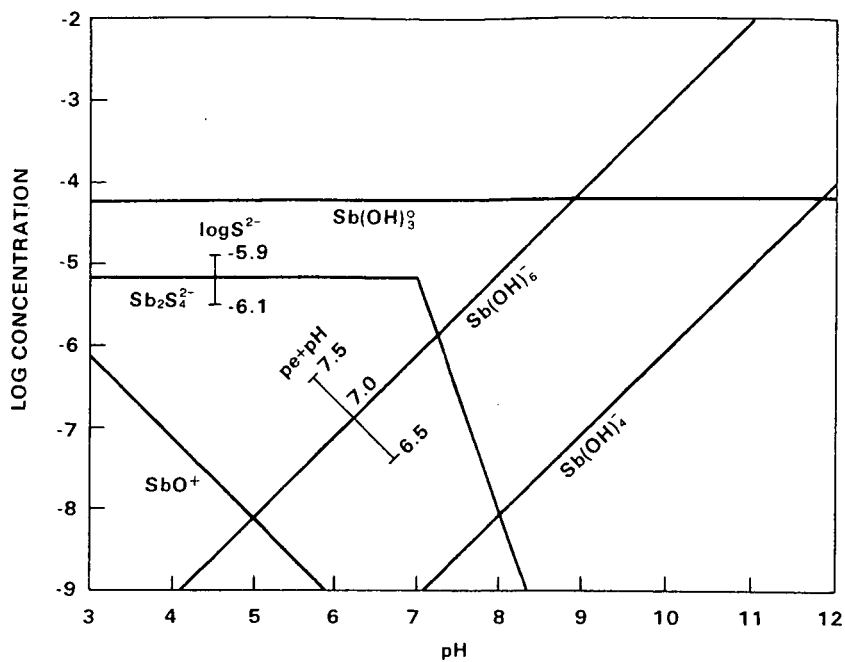


Figure 4-2. The activities of Sb(III) aqueous species along with a Sb(V) species [Sb(OH)_6^-] in equilibrium with $\text{Sb}_2\text{O}_3(\text{c})$.

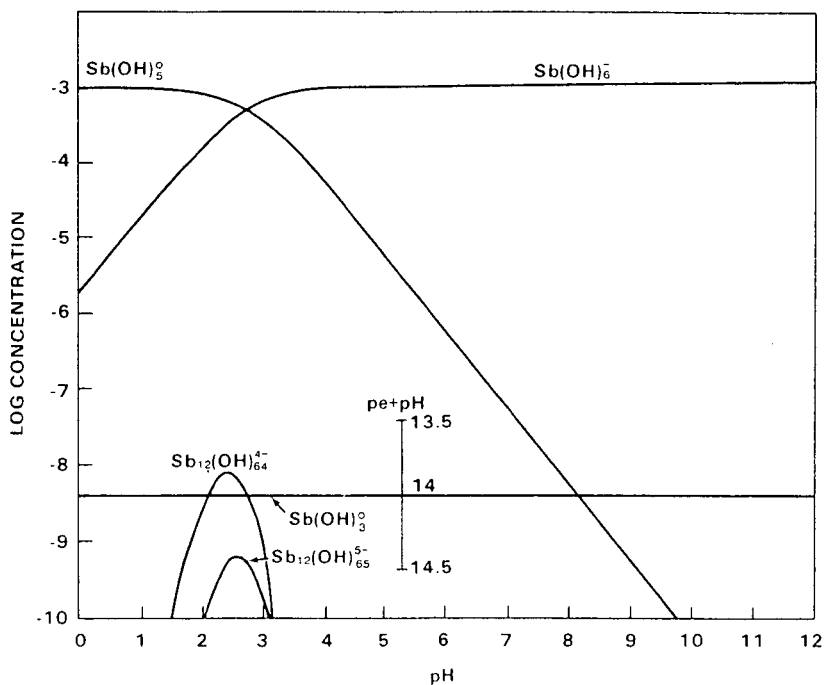


Figure 4-3. The equilibrium concentration of Sb(V) species in 0.001 M total Sb(V).

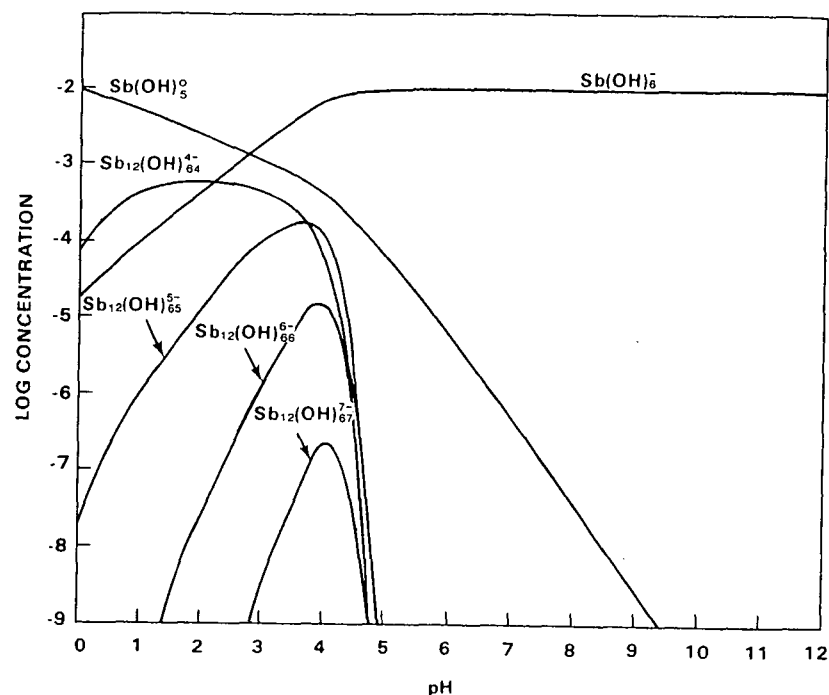


Figure 4-4. The concentration of Sb(V) species in equilibrium with 0.01 M total Sb(V).

which the concentration of the dominant solution species in equilibrium with the least soluble Sb solid phase is plotted as a function of $pe + pH$. The solids are highly soluble in environments with redox potentials greater than $pe + pH$ of 10. Even at $pe + pH < 10$, the solubility of Sb_2O_3 is fairly high ($10^{-4.2}$ M). The antimony-sulfide solid, Sb_2S_3 , will not likely form because the S^{2-} concentrations necessary to precipitate the solid will also form very high concentrations of the solution species $Sb_2S_4^{2-}$.

PRECIPITATION/DISSOLUTION

Although very limited literature is available for Sb behavior in the environment, all of the known Sb solids are fairly soluble. Thus, it appears that Sb concentrations in geologic environments may primarily be controlled by adsorption/desorption reactions rather than precipitation/dissolution.

ADSORPTION/DESORPTION

Little is known of the adsorptive behavior of Sb in soil, subsoil, or ground water, though preliminary studies suggest it is a mobile constituent under diverse environmental conditions (Shvartsev et al. 1974; Ames and Rai 1979). Antimony has been

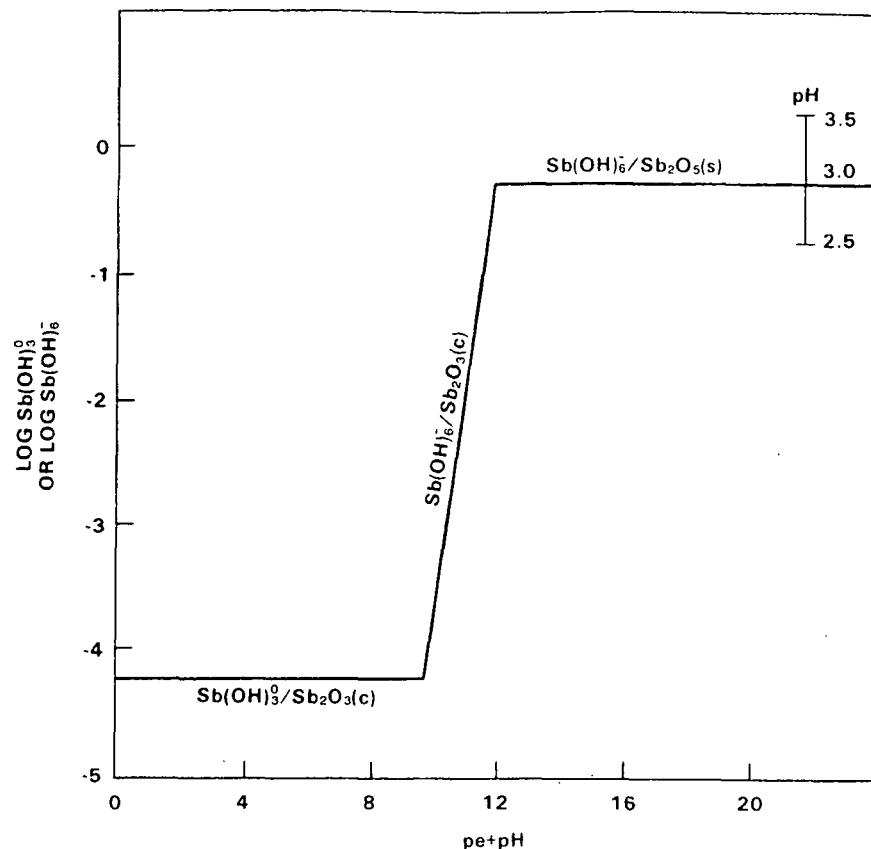


Figure 4-5. The effects of redox potential ($pe + pH$) on the solubility of $Sb_2O_3(c)$ and $Sb_2O_5(s)$ and the nature of dominant aqueous species.

used as an indicator species in hydrogeochemical prospecting because of its high mobility in various geochemical settings from oxygenated to highly reduced waters (Shvartsev et al. 1974). The two valence states [Sb(III), Sb(V)] are found primarily in solution as neutral and negatively charged species $[Sb(OH)_3^0]$, $[Sb(OH)_6^-]$ over the pH range of about 3 to 12 (Figure 4-1). Low adsorption (K_d) is observed in soil from high salt, high pH solutions (Ames and Rai 1979).

Migration has been rapid through soils following spillage of nuclear fuel reprocessing wastes (Haney and Linderorth 1959, Haney 1967, Magno et al. 1970). Adsorption may become more significant under weakly acidic (pH 4 to 5.5) soil/subsoil or ground water conditions where amphoteric hydrous oxides are positively charged, encouraging adsorption of anionic Sb components. Considerable research is needed to define the magnitude of Sb adsorption from utility waste leachates under diverse subsurface conditions.

Section 5

ARSENIC

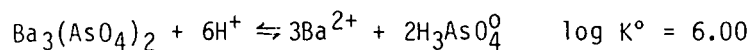
Arsenic (As) in aqueous solutions exists in the +3 and +5 oxidation states. Arsenic(V) species are dominant in oxidizing conditions and occupy a large stability field. Except for an As(III) species (H_3AsO_3^0), all of the dominant As(V) and As(III) species are anions.

Attenuation mechanisms, especially precipitation/dissolution, are not well understood. The available data indicate a strong affinity of As for hydrous oxides. FeAsO_4 has been suggested as a possible solubility-controlling solid. Arsenic is also specifically adsorbed by hydrous oxides of Al and Fe.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIES

Arsenic, a multivalent element, exists in nature in the -3, 0, +3, and +5 valence states. However in aqueous solution, +3 and +5 are the only important states. A predominance-area diagram for As solution species based on thermodynamic data (Ball et al. 1980) in the MINTEQ geochemical model (Felmy et al. 1983) is given in Figure 5-1. The outlined areas represent the pe - pH conditions under which the indicated species are predominant. In general, As(V) species [H_3AsO_4^0 , H_2AsO_4^- , HASO_4^{2-} , AsO_4^{3-}] are dominant in oxidizing environments and occupy a relatively larger stability field than the As(III) species [H_3AsO_3^0 , H_2AsO_3^- , HASO_3^{2-} , AsO_3^{3-}].

The thermodynamic data reported in Table A-2 and in the MINTEQ data base indicate that most reported solid phases of As have very high solubility. However, the solubility of $\text{Ba}_3(\text{AsO}_4)_2$ as reported in MINTEQ and as expressed by the following equation is low.



The corresponding reaction for $\text{Ca}_3(\text{AsO}_4)_2$ has a $\log K^\circ = 22.3$, suggesting that the solubility product for $\text{Ba}_3(\text{AsO}_4)_2$ may be erroneous. The equilibrium constant for $\text{Ba}_3(\text{AsO}_4)_2$ reaction above was quoted by Chukhlantsev (1956); unfortunately, no data were presented to allow us to check the results. Therefore, solid phase solubility diagrams were not developed.

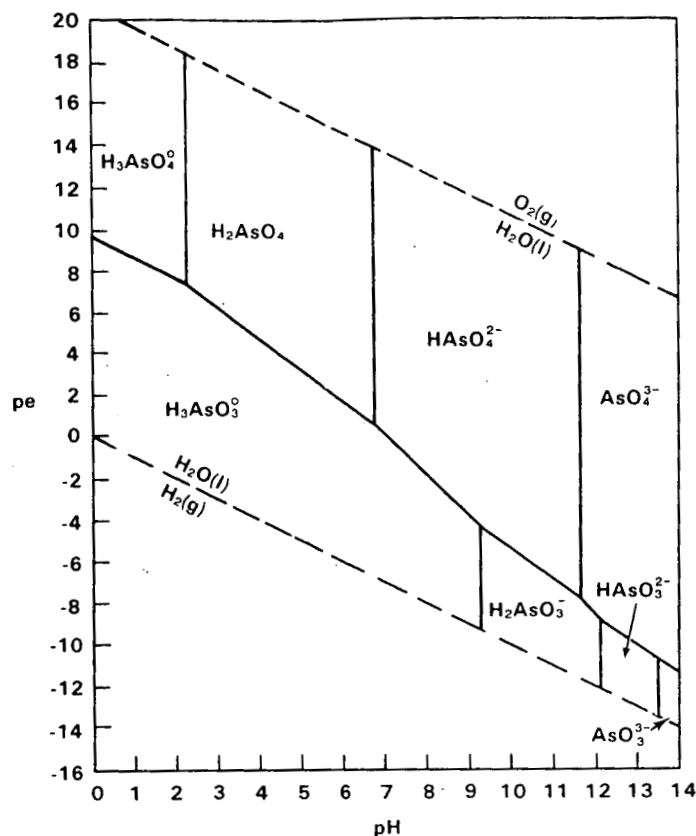


Figure 5-1. The pe-pH diagram for As-H₂O system, at 25°C.

To determine the dominant As aqueous species under oxidizing ($pe + pH = 16$) and relatively reducing conditions ($pe + pH = 7$), total concentration of As in solution was assumed to be 10^{-6} M. Under oxidizing conditions, $H_2AsO_4^-$ and $HAsO_4^{2-}$ are the important As species with $H_3AsO_4^0$ and AsO_4^{3-} also becoming important at $pH < 4.5$ and $pH > 9.25$, respectively (Figure 5-2). Under reducing conditions, the important aqueous species are $H_3AsO_3^0$, $HAsO_3^{2-}$, and $H_2AsO_3^-$ (Figure 5-3).

PRECIPITATION/DISSOLUTION

Precipitation/dissolution reactions of As in soils and sediments have not been extensively studied. Although several investigators suggest that different arsenic compounds may be important in controlling aqueous As concentrations, these predictions are yet to be confirmed. Ferguson and Gavis (1972) predicted that As sulfides (AsS or As_2S_3) would control As concentrations in solutions of low redox and acidic pH. $FeAsO_4$ was expected to control As levels at high redox ($pe > 12.5$) and acidic pH ($pH < 2.3$). Ferguson and Gavis (1972) supported the hypothesis of

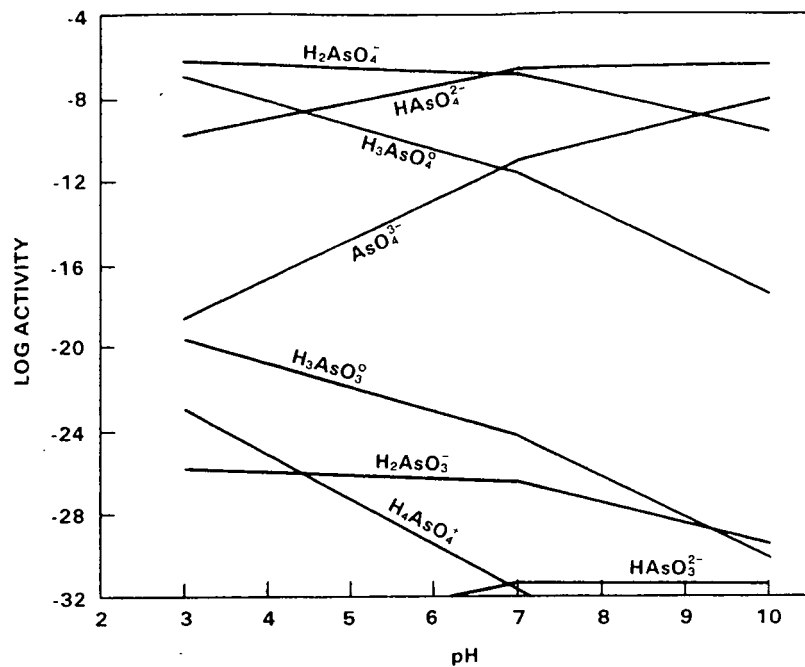


Figure 5-2. Activities of As aqueous species at $\text{pe} + \text{pH} = 16$ when total concentration of soluble As is assumed to be 10^{-6} M.

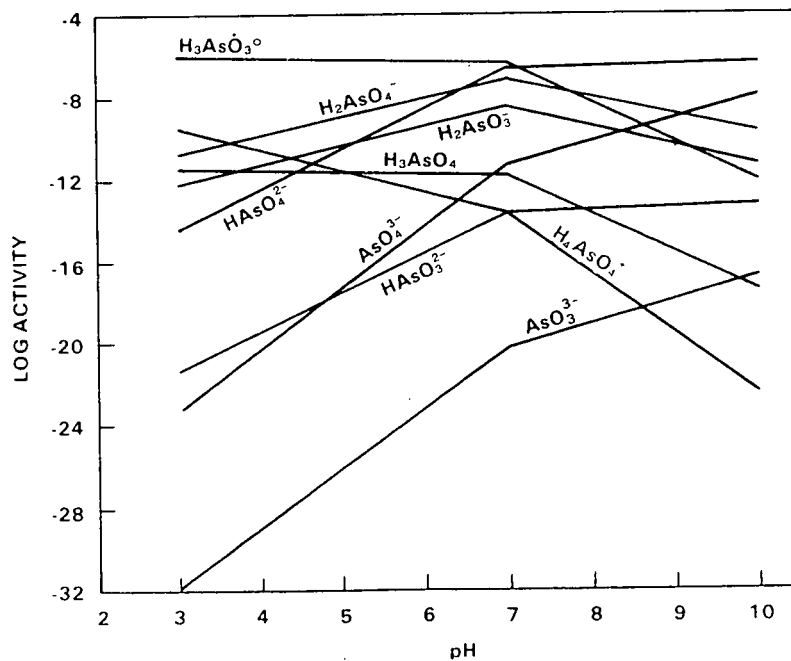


Figure 5-3. Activities of As aqueous species at $\text{pe} + \text{pH} = 7$ when total concentration of soluble As is assumed to be 10^{-6} M.

$\text{FeAsO}_4(\text{s})$ precipitation by citing that iron ores tend to be enriched in As. Hess and Blancher (1977) measured As levels in soils over a wide range of redox and pH values and provided some evidence that $\text{Pb}_3(\text{AsO}_4)_2$ or $\text{Mn}_3(\text{AsO}_4)_2$ may be controlling As levels. This type of solubility-controlling solid phase was expected to be highly dependent upon Eh and pH conditions. Benjamin and Bloom (1981) observed that the adsorption of AsO_4^{3-} and AsO_3^{3-} onto ferric oxyhydroxide enhanced adsorption of trace metal cations (e.g., Cd). Benjamin and Bloom (1981) suggested that a Fe-As solid phase could be forming on the surface of the ferric oxyhydroxide, and the presence of this new solid was responsible for the enhanced adsorption. Livesey and Huang (1981) measured the ionic activity products for the Al, Fe(III), Ca, Mg, Mn, and Pb arsenates and found that soil solution levels of AsO_4^{2-} were far below saturation limits for all arsenates. Livesey and Huang (1981), therefore, concluded that adsorption, not precipitation, controlled AsO_4^{2-} levels in soils.

ADSORPTION/DESORPTION

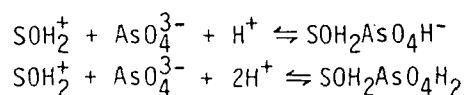
Studies of As retention by soil have shown that adsorption is controlled to a large degree by the content of extractable amorphous/cryptocrystalline hydrous oxides of Fe and Al (Jacobs et al. 1979, Wauchope 1975, Livesey and Huang 1981). Soil organic carbon content and pH do not demonstrate marked correlation with As adsorption in soil. Adsorption studies with a number of pure phase mineral materials have shown that Fe- and Al-oxide have a high capacity, on the basis of surface area, for As (Table 5-1) (Ferguson and Anderson 1974, Anderson et al. 1976, Pierce and Moore 1980, Gupta and Chen 1978, Leckie et al. 1980, Wangen et al. 1982) relative to layer lattice silicates (Frost and Griffin 1977a, Huang 1975). Arsenic, like phosphate, is strongly adsorbed by most soils and sediments. While the adsorption of As(V) as arsenate (AsO_4^{3-}) is comparable to PO_4^{3-} (Wauchope 1975, Holm et al. 1979), As(III) retention on sediments or on Al- and Fe-oxide as arsenite (AsO_3^{3-}) is significantly less (Gupta and Chen 1978, Ferguson and Anderson 1974, Holm et al. 1979).

Although not widely correlated with soil pH, As adsorption on amorphous and crystalline hydrous oxides and layer lattice silicates exhibits marked pH dependency (Table 5-1) and suggests high mobility of As under alkaline conditions. On Al and Fe oxides, maximum adsorption of As(III) occurs between pH 7 to 9 (Pierce and Moore 1980, Gupta and Chen 1978). While adsorption of As(V) is high and independent of pH at low pH, adsorption decreases with increasing pH (pH 7 to 9) (Anderson et al. 1976, Leckie et al. 1980). The pH of the adsorption edge and maxima are a complex function of the pK_a of the acid anion(s), the adsorbing species, the adsorption stoichiometry and surface charge characteristics (Anderson et al. 1976, Leckie et al. 1980, Anderson and Malotky 1979). In general, adsorption decreases as the

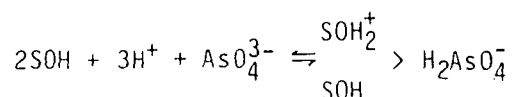
solution pH increases and surface positive charge decreases toward the pH of the isoelectric point (pH_{IEP}) of the adsorbent. Experimental evidence indicates that As adsorption reduces net surface charge and the pH_{IEP} (Anderson et al. 1976, Anderson and Malotky 1979). Both the pH_{IEP} and the adsorption edge move to lower pH with increasing adsorption density. The presence of certain competing anions and complexing ions may affect As adsorption (Table 5-1). Phosphate strongly competes with As for adsorption sites on iron oxides (Hingston et al. 1971), soils (Livesey and Huang 1981, Barrow 1974b), and sediments (Holm et al. 1979). Other anions (e.g., NO_3^{2-} , Cl^- , and SO_4^{2-}), even when present in great excess, have little effect (Livesey and Huang 1981, Leckie et al. 1980). The adsorption of As ion pairs (e.g., $CaHAsO_4$, KH_2AsO_4) and complexes (e.g., $CuHAsO_4$) by iron hydroxides may increase As removal from fly ash leachate over that predicted from As activity alone (Leckie et al. 1980).

Over realistic environmental concentration ranges (10^{-4} to 10^{-7} M), As adsorption conforms to single (oxides, sediments) and multiple site (soils) Langmuir adsorption equations. Langmuir constants determined for single mineral phases exhibit pH dependency (Pierce and Moore 1980, Anderson et al. 1976) with maxima for As(III) and V) on Fe and Al oxides occurring near pH 7 (Table 5-1). The Langmuir adsorption maxima for As(III) on amorphous iron oxyhydroxide and As(V) on amorphous aluminum hydroxide are quite high (450 to 600 μ moles/g) and exceed the few reported values for soil by several orders of magnitude (Table 5-1).

A number of chemical reactions have been used to successfully model pH-dependent As adsorption on oxide and hydrous oxide minerals. The adsorption of As(V) on amorphous oxyhydroxide can be described by simultaneous solution of two reactions (Leckie et al. 1980, Benjamin and Bloom 1981)



In contrast, the formation of one bidentate complex is adequate to simulate As adsorption on $Al(OH)_3_{am}$



These reactions are consistent with experimental observations of pH increase (proton consumption), reduction in net surface positive charge, and poorly reversible adsorption on $\text{Al}(\text{OH}_3)_{\text{am}}$.

Other arsenic species may, in select instances, be of environmental significance. These include salts of methanearsonic acid (MA) or cacodylic acid (hydroxy dimethylarsine oxide, CA) which were used extensively in the past as herbicides and defoliants. Cacodylate may also be formed by anaerobic microbial processes from arsenate or methanearsonate via formation, and subsequent air oxidation, of dimethylarsine (Braman and Foreback 1973, Cox and Alexander 1973). The adsorption behavior of MA and CA in soil and sediment are similar to arsenate, with cacodylic acid being less strongly adsorbed (Holm et al. 1979, Wauchope 1975). In sediment, the adsorption of As(III) is comparable to cacodylic acid.

Table 5-1. ADSORPTION CONSTANTS FOR ARSENIC

Adsorbent		Adsorbate		Electrolyte			Adsorption Measurements		Reference
Identity	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (a)	Value	
Amorphous Iron oxyhydroxide Fe ₂ O ₃ ·H ₂ O(am)	-	183	10 ^{-6.3} As(V)	NaNO ₃	0.1	3-12	K ^{Int} HAsO ₄	9.3	Leckie et al. 1980
			10 ^{-4.3} As(V)				K ^{Int} HAsO ₄	8.40	
			10 ^{-6.3} - 10 ^{-4.3} As(V)				K ^{Int} H ₂ AsO ₄	7.48	
Amorphous Iron oxyhydroxide, Fe ₂ O ₃ ·H ₂ O(am)	-	183	10 ⁻³ - 10 ⁻⁴ As(V)	NaNO ₃	0.1	3-12	K ^{Int} HAsO ₄	11.1	Benjamin and Bloom 1981
							K ^{Int} H ₂ AsO ₄	9.90	
Amorphous aluminum hydroxide, Al(OH) ₃ (am)	-	500	10 ^{-4.2} - 10 ^{-3.1} As(V)	NaClO ₄	0.01	3.5- 10.5	β ^{Int} H ₂ AsO ₄	11.9	Davis 1978
Amorphous aluminum hydroxide, Al(OH) ₃ (am)	-	500	10 ^{-4.2} - 10 ^{-3.1} As(V)	NaClO ₄	0.01	5	A _m , K _L	1600, 5.08	Anderson et al. 1976
						6		1478, 5.17	
						7		1179, 5.24	
						8		838, 5.12	
						8.5		681, 4.85	
						9		501, 4.62	

Table 5-1 (Contd). ADSORPTION CONSTANTS FOR ARSENIC

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		Reference
Identity	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (a)	Value	
Amorphous oxyhydroxide, Fe ₂ O ₃ ·H ₂ O	-	-	10 ⁻⁷ - 10 ⁻⁵ As(III) as AsO ₂ ⁻	NaNO ₃	1.0				Pierce and Moore 1980
						4.0	A _m , K _L	457, 5.98	
						5.0		463, 6.18	
						5.7		490, 6.26	
						6.1		503, 6.33	
						7.0		513, 6.36	
						8.0		488, 6.30	
						8.8		417, 6.18	
Activated bauxite	-	-	10 ⁻⁵ - 10 ⁻⁴ As(V)	Water	-	6-7	As(III) A _m , K _L	16, 5.16	Gupta and Chen 1978
							As(V) A _m , K _L	52, 6.39	
			10 ⁻⁶ - 10 ⁻⁵ As(III)	Seawater	0.07 (1:10/dil)	6-7	As(III) A _m , K _L	16, 5.02	
							As(V) A _m , K _L	44, 6.07	
			+	NaCl	0.67	6-7	As(III) A _m , K _L	17, 4.93	
							As(V) k	59, 5.56	
				Seawater	0.7	6-7	As(III) A _m , K _L	1.0, 5.10	
							As(V) A _m , K _L	33, 5.54	

Table 5-1 (Contd). ADSORPTION CONSTANTS FOR ARSENIC

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		
Identity	CEC meq/100g	S ₂ A _s m ² /g	Conc., M	Identity	Conc., M	pH	Constants ^(a)	Value	
Activated alumina	-	210	10 ⁻⁵ - 10 ⁻⁴ As(VI) +	Water		6-7	As(III) A _m , K _L	14, 5.54	Gupta and Chen 1978
							As(V) A _m , K _L	67, 6.85	
			10 ⁻⁶ - 10 ⁻⁵	Seawater	0.7 (1:10/dl)	6-7	As(III) A _m , K _L	19, 4.98	
							As(V) A _m , K _L	230, 5.30	
				NaCl	0.67	6-7	As(III) A _m , K _L	14, 5.37	
							As(V) A _m , K _L	140, 5.46	
Kaolinite	15.1	34.2	10 ⁻⁴ - 10 ⁻² As(V) +	Leachate		5	As(V) A _m , K _L	7.19, 3.54	Frost and Griffin 1977
			10 ⁻⁴ - 10 ⁻³ As(III)						
Montmorillonite	79.5	86.0	10 ⁻⁴ - 10 ⁻³ As(V) +	Leachate		5	As(V) A _m , K _L	9.9, 3.57	
			10 ⁻⁴ - 10 ⁻³ As(III)						

Table 5-1 (Contd). ADSORPTION CONSTANTS FOR ARSENIC

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		Reference
Identity	CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants ^(a)	Value	
<u>Hydroxy Al-coated muscovite</u>									
2-5 μm	-	-	10 ⁻⁴ - 10 ⁻³	NaCl	0, 0.1, 1.0	6-7	A _m , K _L	12.0, 1.91	Huang 1975
0.2-2 μm	-	-	As(V)					22.6, 1.64	
0.08-0.2 μm	-	-						58.7, 1.22	
<0.08 μm	-	-						66.7, 1.17	
<u>Hydroxy Al-coated biotite</u>									
2.5	-	-	10 ⁻⁴ - 10 ⁻³	NaCl	0, 0.1, 1.0	6-7	A _m , K _L	8.01, 2.07	
0.2-2 μm	-	-	As(V)					12.0, 1.89	
0.08-0.2 μm	-	-						55.6, 1.25	
<0.08 μm	-	-						65.4, 1.18	
<u>Soils</u>									
Clay-8.0%, Org C-2.96%	-	-	10 ⁻⁶ - 10 ⁻⁵	-		7	A _m (I), A _m (II), Total	0.32, 2.99, 3.31	Wangen et al. 1982
			As(V)	-		7	A _m (I), A _m (II), Total	0.80, 3.67, 4.47	
Clay-42.2%, Org C-4.98%	-	-		-		7.5	A _m (I), A _m (II), Total	0.88, 2.67, 3.55	
Clay-23.3%, Org C-2.03%	-	-		-		5.9	A _m (I), A _m (II), Total	0.37, 3.23, 3.60	
Clay-14.9%, Org C-2.45%	-	-		-					

(a) K^{int}, β^{int} = intrinsic adsorption constants of ionic species, log

K_L = Langmuir constant, log M⁻¹

A_m = Langmuir adsorption maximum, μmol g⁻¹

A_m(I), A_m(II) = two adsorption sites

Section 6

BARIUM

Like other alkaline earth cations, barium (Ba) in aqueous environments exhibits only +2 valence state. At pH values <9.3, Ba^{2+} is the dominant species with BaSO_4^0 becoming important in groundwaters with high sulfate concentrations. Both amorphous and crystalline forms of barite (BaSO_4^0) may form in subsurface environments, but Ba solution concentrations are expected to be controlled primarily by ion exchange reactions. Barium is more strongly adsorbed than Sr, Ca, and Mg by most layer lattice clays and soil hydrous oxides.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIES

Barium in aqueous solutions exhibits only +2 valence state. Barite and witherite (BaCO_3) have fast precipitation kinetics and are the compounds that may form in surficial deposits and limit maximum possible Ba concentrations in waters.

To determine the relative abundance of Ba(II) species in ground waters representative of utility waste environments, activities of different Ba aqueous species in equilibrium with barite and witherite were plotted using the thermodynamic data (Ball et al. 1980) contained in the geochemical model MINTEQ (Felmy et al. 1983) and in Table A-3. Under the assumed conditions (Figure 6-1), Ba^{2+} followed by BaSO_4^0 is the dominant aqueous species in groundwaters of pH values ≤ 9.3 . At pH values > 9.3 , BaCO_3^0 species are dominant. Ba^{2+} forms relatively weak complexes with Cl^- , OH^- , and NO_3^- ; hence, these complexes do not contribute significantly to total Ba concentration. Figure 6-1 also shows that barite is more stable than witherite in a large pH range and that witherite can only be expected to be stable in very alkaline conditions.

PRECIPITATION/DISSOLUTION

Although very limited data exists on Ba geochemical behavior, most alkaline earth elements such as Ba are generally expected to be controlled by adsorption-desorption reactions. As mentioned above, witherite (in highly alkaline conditions) and barite may, in some instances, control Ba concentrations in natural waters or leachates.

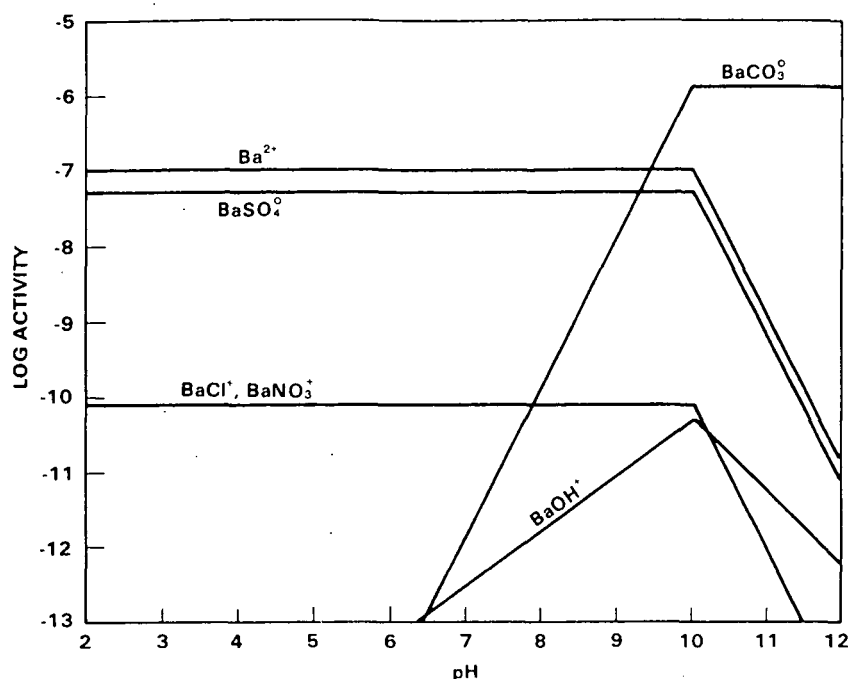


Figure 6-1. Activities of different barium species when Ba^{2+} activity is controlled by barite (BaSO_4) or witherite (BaCO_3) and when $\text{Cl}^- = \text{SO}_4^{2-} = 10^{-3.4}$, $\text{NO}_3^- = 10^{-4}$, and $\text{CO}_2(\text{gas}) = 10^{-3.52}$ atmospheres.

Jenne et al. (1980) working with waters from Missouri tri-state Pb- and Zn-mining area, report that barite appears to control Ba concentrations.

ADSORPTION/DESORPTION

Specific and nonspecific adsorption of Ba has been observed on soil and in model adsorbents (Table 6-1). Electrostatic or coulombic forces (nonspecific adsorption) account for a large fraction of adsorption in soil and subsoil. Thus, like other alkaline earth cations, Ba retention is controlled, to a large extent, by the cation exchange capacity of the adsorbent. The relative affinity of alkaline earth cations for cation exchange and specific adsorption sites on most clay minerals, oxides, and hydrous oxides decreases in the order $\text{Ba} > \text{Sr} > \text{Ca} > \text{Mg}$, thus reflecting a decreasing ionic (dehydration) radius through the series (Table 6-2). Complexation by soil organic material occurs to a limited extent (Broadbent and Ott 1957).

Specific adsorption of Ba^{2+} and other alkaline earth cations does occur to some degree on oxide and hydrous oxide minerals in soil, which is accompanied by proton release (Kinniburgh et al. 1976, Murray 1975). However, Ba may adsorb without

releasing protons, and thus, react electrostatically with points of negative charge. The order of affinity which alkaline earth cations have for various oxides is consistent with the electrostatic properties of the solids and the energy of hydrolysis of the cations (Table 6-2). The log hydrolysis constants of Mg, Ca, Sr, and Ba are 2.58, 1.32, 0.88 and 0.69, respectively. Their ionic radii are 0.65, 0.99, 1.13 and 1.35 Å. The relative affinity depends on the surface charge density and net sign of the oxide surface which, in turn, is a function of pH and electrolyte concentration, the relative size (or charge density) and the degree of hydrolysis of the cation. The data in Table 6-2 indicate that Ba will displace other adsorbed alkaline earths from MnO_2 , SiO_2 , and TiO_2 under usual environmental conditions, while Ba on Al_2O_3 will be displaced by other alkaline earths.

Table 6-1. ADSORPTION CONSTANTS FOR BARIUM

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurement		Reference
Identity	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (a)	Value (b)	
<u>Clay Minerals</u>									
Montmorillonite,									
NH ₄ -saturated	-	-	-	ΣCl ⁻	0.1	<5	ΔG ^{oBa} _{NH₄}	(4.7)	Elprince et al. 1980
La-saturated	-	-	-	ΣCl ⁻	0.1	<5	ΔG ^{oBa} _{La}	(9.4)	
<u>Alumina</u>									
Al oxide gel									
fresh	-	-	10 ^{-3.6}	NaNO ₃	1.0	10.5	A	17	Kinniburgh et al. 1976
aged	-	-	10 ^{-3.6}	+ Mg ²⁺ , Ca ²⁺ and Sr ²⁺	10 ^{-3.6} each	11.2	A	17	
Hydrous γ-Al ₂ O ₃	-	117	-	NaCl	0.1	-	K ^{Ba} _H ΔG ^o _{ads}	-6.59 2.5	Huang and Stumm 1973
Hydrous γ-Al ₂ O ₃	-	-	-	-	-	-	*K ^S _I K ^{Int} _{K²⁺} Ba ²⁺	-6.6 (2.9)	Stumm et al. 1976

Table 6-1 (Contd). ADSORPTION CONSTANTS FOR BARIUM

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurement		References
Identity	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (a)	Value (b)	
<u>Fe Oxides</u>									
Fe oxide gel	-	-	10 ^{-3.0}	NaNO ₃	1.0	7.55	A	60	Kinniburgh et al. 1976
			10 ^{-3.6}	NaNO ₃	1.0	7.25	A	17	
				Mg ²⁺ , Ca ²⁺ and	10 ^{-3.6} each				
				Sr ²⁺					
<u>Mn Oxides</u>									
Hydrous MnO ₂	-	-	10 ⁻⁵ - 10 ⁻³	NaClO ₄	0.01	5	A _m , K _L	2050, 4.6	Posselt et al. 1968
<u>Ti Oxides</u>									
Rutile	-	26	10 ⁻³	-	-	8.6	A ΔG ^o _{ads}	77 -8.6	Stumm et al. 1976
<u>Sediment</u>									
River	-	-	10 ^{-5.9}	Seawater	~0.7	8	A K _d	1.0 530	Li and Chan 1979
River	-	-	10 ^{-6.4}	River water	-	-	K _d	2800	

(a) ΔG_M^{oBa} = free energy of exchange, cal mol⁻¹
A = adsorption, $\mu\text{mol g}^{-1}$

K_M^{Ba} = exchange coefficient, log

ΔG_{ads}^o = free energy of adsorption, kcal mol⁻¹

* K_1^s = surface complexation constant, log

K^{Int} = intrinsic adsorption constant, log

K_d = distribution coefficient, ml g⁻¹

(b) () = estimate value

Table 6-2

ALKALINE EARTH CATION AFFINITY FOR OXIDES

<u>Oxide</u>	<u>pH_{zpc}</u>	<u>Order of Affinity</u>	<u>References</u>
MnO ₂	~2.6	Ba > Sr > Ca > Mg	Posselt et al. 1968, Murray 1975
SiO ₂	~4.2	Ba > Sr > Ca > Mg	Stumm et al. 1976
TiO ₂	5.8	Ba > Sr > Ca > Mg	Fuerstenau et al. 1981
FeOOH	7.8	Ba > Ca > Sr > Mg (pH < 8)	Kinniburgh et al. 1976
Al ₂ O ₃	8.6	Mg > Ca > Sr > Ba	Kinniburgh et al. 1976 Huang and Stumm 1973

Section 7

BERYLLIUM

Beryllium (Be) in aqueous environments exists in +2 valence state. Fluoro- and hydroxo- complexes of Be appear to be the dominant aqueous species at pH values of approximately <6 and >6, respectively. Essentially no data are available on precipitation/dissolution and adsorption attenuation mechanisms. The available thermodynamic data suggests that β -Be(OH)₂(c) has fairly low solubility; additionally, β -Be(OH)₂ has fast precipitation kinetics and may be an important concentration-limiting solid phase.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIES

Beryllium only exhibits a +2 valence state. The selected thermodynamic data for Be species are reported in Table A-4. The relative stability of some of the Be solid phases for which the thermodynamic data are available are plotted in Figure 7-1. Chloride, fluoride, and sulfate compounds of Be are too soluble and fall outside the graph boundaries. Among the solid phases reported in Figure 7-1, phenakite (BeSiO₄) is the most stable solid followed by chrysoberyl (BeAl₂O₄) and β -Be(OH)₂. Phenakite and chrysoberyl form under high temperatures and pressures. Information about other Be solids that may form in surficial environmental conditions is not available.

Information regarding the dominant aqueous Be species under a range in activities of complexing ligands and the solubility of phenakite can be obtained from Figure 7-2. Depending upon the fluoride content of the waters, Be in low pH (<5.5) waters would be present as Be²⁺ or BeF⁺. At pH values between 5.5 and 8.2, and 8.2 and 9.6, BeOH⁺ and Be(OH)₂⁰, respectively, are expected to be the dominant species. It should, however, be pointed out that the thermodynamic data used for Be(OH)₂⁰ species are questionable (Smith and Martell 1976); there is some uncertainty about the values of formation constants of Be with fluorides. The data show that the chloride, nitrate, sulfate, and polynuclear hydrolysis species of Be do not contribute significantly to the total soluble Be. Information on carbonate complexes of Be is not available, so the importance of carbonate complexation in alkaline waters cannot be assessed. The relative activity of different species in equilibrium with β -Be(OH)₂ would be two orders of magnitude higher than those shown for phenakite (Figure 7-2).

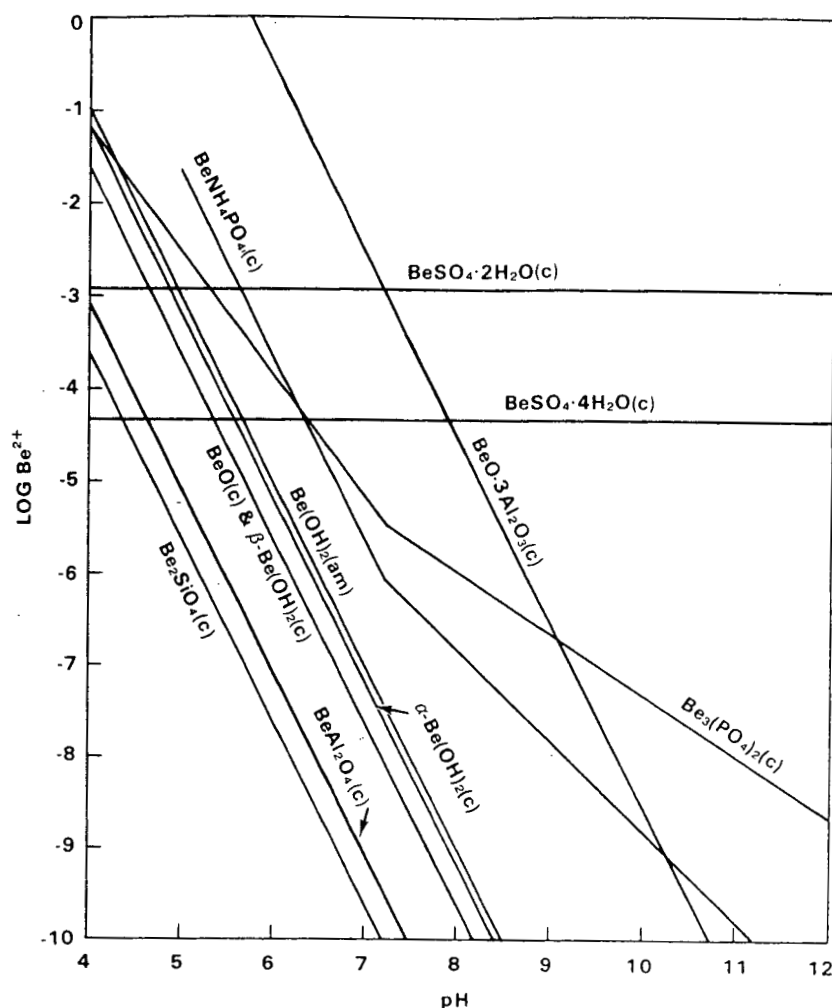


Figure 7-1. Relative solubility of Be solid phases when $\text{SO}_4^{2-} = 10^{-3.0}$, $\text{H}_2\text{PO}_4^- = 10^{-5.5}$ (at pH values <7.2) and $\text{HPO}_4^{2-} = 10^{-5.5}$, Al activity is controlled by $\gamma\text{Al}(\text{OH})_3(\text{c})$ and the Si activity by $\text{SiO}_2(\text{am})$.

PRECIPITATION/DISSOLUTION

Merrill et al. (1960) and Udodov and Parilov (1961) report 0.5 to 17 $\mu\text{g/l}$ ($10^{-5.7}$ to $10^{-7.3}$ M) Be in surface waters. Machacek et al. (1966) reports similar Be concentrations (0.5 to 0.78 $\mu\text{g/l}$) in ground waters. It is interesting that the concentrations in surface waters are similar to Be concentrations predicted from chrysoberyl or $\beta\text{-Be}(\text{OH})_2$. Information was not found on the Be compounds that could form in the geologic environments and/or that could control Be concentrations in solutions. Most of the available information is either of a general nature only

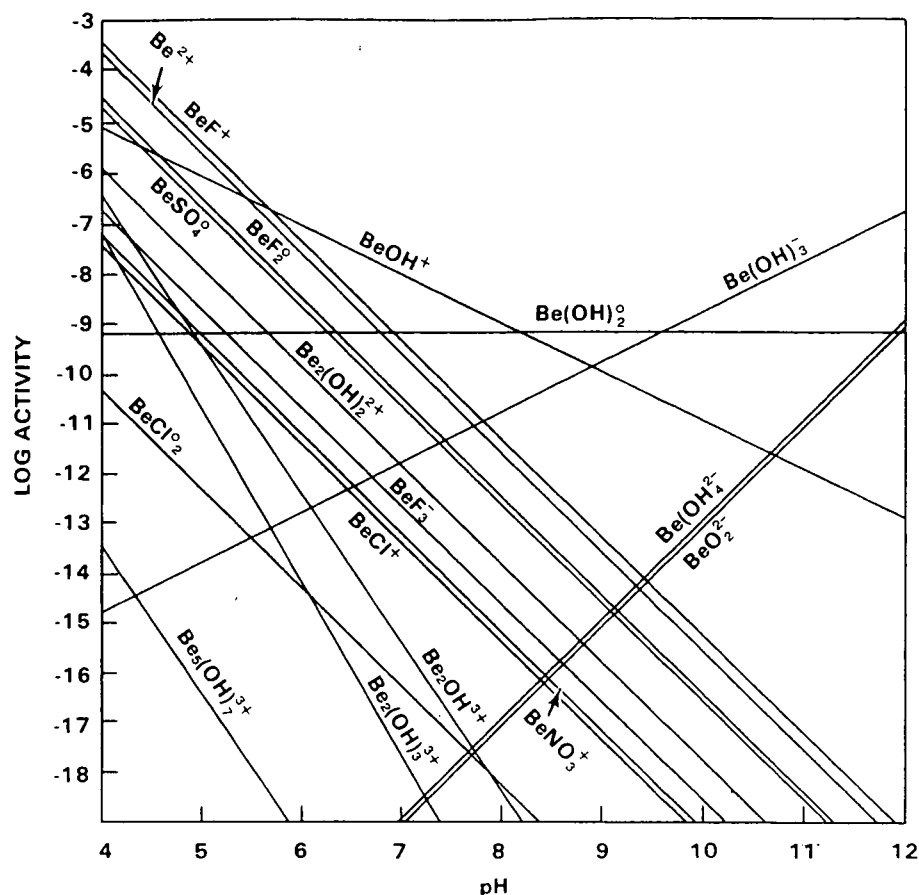


Figure 7-2. The activities of Be aqueous species in equilibrium with $\text{Be}_2\text{SiO}_4(\text{c})$ and $\text{SiO}_2(\text{am})$ and when $\text{SO}_4^{2-} = \text{Cl}^- = \text{NO}_3^- = 10^{-3.0}$ and $\text{F}^- = 10^{-5.0}$.

where concentrations of total Be were determined in different solid materials and waters, or the predictions of solution species were based on the thermodynamic data. To study the Be aqueous behavior, Karlander and Krauss (1972) studied the effect of pH on Be precipitation in algal medium. The authors were unable to ascertain whether the change in Be concentrations from $10^{-4.1} \text{ M}$ at pH 5 to about $10^{-4.8} \text{ M}$ at pH 8 was due to precipitation or adsorption by algal medium. However, the data presented in Figures 7-1 and 7-2 suggest that this change may have been due to precipitation of Be(OH)_2 .

ADSORPTION/DESORPTION

Beryllium adsorption in soils has not been well investigated. No literature was found where Be adsorption was the sole topic, although several investigators have studied this element in a cursory manner. Preliminary evidence indicates that Be

adsorption on soils and some layer lattice silicates is pH dependent and that adsorbed Be is not effectively replaced by Ba, Ca, and Mg (Romney and Childress 1965). These alkaline earth cations, however, may compete with Be when simultaneously present in the solution phase (Romney and Childress 1965), suggesting an ion exchange retention mechanism. Beryllium, present in a simulated solid waste leachate, was more strongly attenuated in column studies with 11 soils from seven prominent soil orders than were Zn, Cd, Ni, and Hg (Alesii et al. 1980, Korte et al. 1976). Only Cu and Pb exhibited less mobility than Be. Calcareous soils high in layer lattice silicates appear most effective in Be retention (Korte et al. 1976, Alesii et al. 1980). Information is not available to identify the most important mineral absorbents or the relative importance of ion exchange or specific adsorption mechanisms in Be adsorption by soil.

Section 8

BORON

Boron (B) in aqueous solutions exists as H_3BO_3^0 at pH values of approximately <9.2 and as $\text{B}(\text{OH})_4^-$ at pH values >9.2 . Most of the solid phases of B, for which thermodynamic data are available, are fairly soluble. Therefore, adsorption/desorption reactions are primarily expected to control geochemical behavior of B. Amorphous Al- and Fe-oxides and to a lesser extent 1:1 clay minerals are important adsorbents. The adsorption is greatest under alkaline conditions.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIES

Boron has +3 valence state but does not exist in aqueous solution as a cation. Boron readily hydrolyzes in aqueous solutions and the least hydrolyzed form of B(III) is $\text{B}(\text{OH})_3$ or H_3B_3^0 . Boron forms several alkali and alkaline earth borates. There is, however, a general lack of thermodynamic data for boron solids. Mattigod (1983) calculated solubility products of several borate minerals (pinnoite, inderite, inyoite, colemanite, inderborite, hungchaoite, borax, sborgite, McAllisterite, kaliborite, nobleite) based on the data presented by Bassett (1976) and also proposed a method of estimating the standard free energies of formation of borate minerals. Using Mattigod's (1983) data, the calculated solubilities of alkali and alkaline earth borates were very high suggesting the unlikelihood of these minerals to be the solubility-limiting solids in dilute ground waters.

To determine the relative abundance of B species in ground waters representative of leachates, activities of different B species (when $\text{H}_3\text{BO}_3^0 = 10^{-5} \text{ M}$) were plotted (Figure 8-1) using the thermodynamic data (Ball et al. 1980) contained in the geochemical model MINTEQ (Felmy et al. 1983). Under the assumed conditions (Figure 8-1), H_3BO_3^0 is the dominant aqueous species at pH values <9.2 . At pH values >9.2 , $\text{B}(\text{OH})_4^-$ is the dominant species. In addition to hydroxo complexes of B, information is only available for B complexes with F. However, the data presented in Figure 8-1 indicate that the contribution of B-F complexes [$\text{BF}_2(\text{OH})_2^-$, BF_4^- , BF_3OH^- , $\text{BF}(\text{OH})_3^-$] to the total B concentration is insignificant.

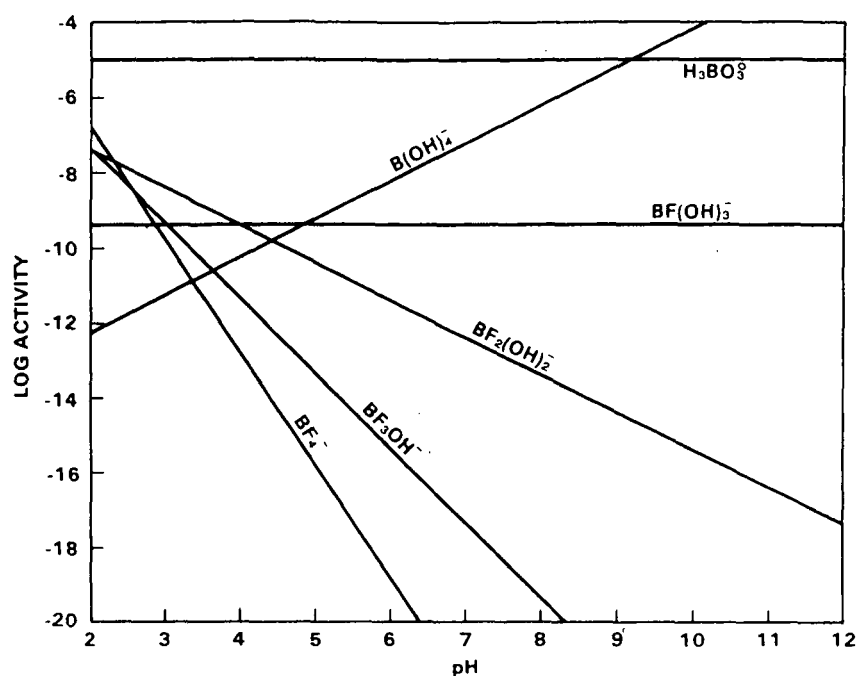


Figure 8-1. Activity of different species when activity of H_3BO_3^0 fixed at 10^{-5} , $\text{F}^- = 10^{-4}$, and $\text{CO}_2(\text{gas}) = 10^{-3.52}$ atmospheres.

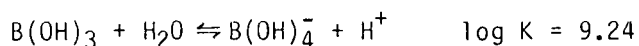
PRECIPITATION/DISSOLUTION

Since most known boron minerals are fairly soluble, adsorption/desorption is expected to control the geochemical behavior of boron. The short-term attenuation of boron by soils, minerals, or other solid phases did not follow a pattern consistent with the precipitation of B solid phases (Keren and Mezuman 1981, Hingston 1964, Hatcher et al. 1967). However, other authors have interpreted the attenuation of B by solids as the formation of B solids. Parks and Shaw (1957) showed that B may be precipitated in combination with Al^{3+} and H_4SiO_4^0 . Biggar and Fireman (1960) suggested that B reacts with soluble aluminum, silicon, or iron to form hydroxy borate on the surface of the respective oxides. The mechanism of precipitation was proposed to be an "exchange" of H_3BO_3^0 or B(OH)_4^- for surface hydroxyls. Couch and Grim (1968) observed the fixation of B into clay minerals and attributed the fixation to the incorporation of B into the clay lattice through a diffusion process. The results of Rhoades et al. (1970a, 1970b) indicate that B concentration in soils were solubility limited. Magnesium-hydroxy clusters and coatings may facilitate coprecipitation of B under semiarid/arid conditions (Rhoades et al. 1970b). Elrashidi and O'Connor (1981) found that B was irreversibly adsorbed in some soils and suggest irreversibility could be attributed to solid phase formation.

ADSORPTION/DESORPTION

The adsorptive behavior of B in soil (Table 8-1) has received considerable research attention because of its importance as an essential micronutrient and a phytotoxic element. In fact, a narrow concentration range exists between concentrations inducing deficiency and toxicity (Berger 1949). Soil adsorption of B has long been recognized as a complex phenomenon differing appreciably from the adsorption of other protolyzeable anions. A number of diverse soil characteristics have consistently been associated with B retention, including: pH (Keren et al. 1981, Sims and Bingham 1968a, 1968b), Al oxides and particularly amorphous Al oxides (Bingham et al. 1971, McPhail et al. 1972, Sims and Bingham 1968a, 1968b; Hatcher et al. 1967), Fe oxides (Sims and Bingham 1967, 1968b; Mezuman and Keren 1981), and CaCO_3 (Hatcher et al. 1967, Okazaki and Chao 1968, Keren and Mezuman 1981). Other indirect measures of soil properties such as clay content and surface area (Biggar and Fireman 1960, Hatcher et al. 1967) and soil salinity (Fleet 1965, Couch and Grim 1968) often correlate with B adsorption.

Boron adsorption displays marked pH dependency (Table 8-1) with maximum adsorption occurring between pH 7.5 and 10 on clay minerals (Keren and Mezuman 1981, Sims and Bingham 1967, Hingston 1964), Al and Fe oxides (Sims and Bingham 1968b, McPhail et al. 1972), soil organic matter (Huettl 1976), and soils (Mezuman and Keren 1981). The pH dependency of B adsorption may be related to the hydrolysis of boric acid:



The borate ion B(OH)_4^- has a much greater affinity for oxide and clay mineral surfaces than B(OH)_3 (Keren et al. 1981). At high pH (>9.5) increasing OH^- concentrations reduce B adsorption by competition for adsorption sites. Adsorption of B is enhanced in the presence of Ca or Mg (Fleet 1965, Hatcher et al. 1967, Couch and Grim 1968, Okazaki and Chao 1968, Rhoades et al. 1970b, Keren and Mezuman 1981) likely resulting from formation of CaB(OH)_4^+ or MgB(OH)_4^+ (Dyrssen and Wedborg 1974) and adsorption on cation exchange sites.

The most important single constituent influencing B adsorption in soil may be amorphous Al_2O_3 (Bingham et al. 1971). The B adsorption capacity of freshly prepared hydrous Al oxide exceeds that of fresh Fe oxide by a factor of 5 to 10 (McPhail et al. 1972, Sims and Bingham 1968a). Coatings of Fe, and particularly Al oxides, on layer lattice silicates may be more important than the clay mineral

itself in B retention (Sims and Bingham 1968b). Liming soil may increase B adsorption by displacement of exchangeable Al^{3+} and formation of $\text{Al}(\text{OH})_3(\text{s})$, an effective adsorbent (Hatcher et al. 1967). Similarly, Mg-hydroxy clusters appear important in B retention in arid regions (Rhoades et al. 1970b). Soil organic matter may also be important in B adsorption. Both cis-diol and γ -hydroxy carboxylic acid functional groups in soil organic matter have been shown to complex B (Huettl 1976, Parks and White 1957).

Limited data indicate that boron adsorbs on sites that are element specific (Bingham and Page 1971), suggesting B adsorption may not be affected by the presence of other anions present in utility waste leachate. Boron adsorption can be described by the Langmuir equation over narrow concentration ranges (Rhoades et al. 1970a, McPhail et al. 1972, Griffin and Burau 1974, Elrashidi and O'Connor 1982) or the Freundlich isotherm over broader concentration gradients (Fleet 1965, Singh 1971, Elrashidi and O'Connor 1982). The pH-dependent adsorption of B on clay minerals (Keren and Mezuman 1981) and soils (Mezuman and Keren 1981) has been adequately described using a modified competitive Langmuir equation incorporating boric acid hydrolysis, where $\text{B}(\text{OH})_3^0$, $\text{B}(\text{OH})_4^-$, and OH^- are the adsorbing species.

The adsorption behavior of B in soils is further complicated by conflicting data describing its desorption. Adsorption appears to be easily reversible for some soils and soil components (Hatcher and Bower 1958, Hingston 1964, Keren and Gast 1981); however, other soils demonstrate marked hysteresis in desorption (Okazaki and Chao 1968, Rhoades et al. 1970a, Elrashidi and O'Connor 1982). Wetting and drying cycles not only increase the B adsorption capacity (Biggar and Fireman 1960) but render a substantial portion irreversibly adsorbed (Keren and Gast 1981).

Irreversible adsorption may reflect solid phase formation or fixation by clay minerals. Displacement of exchangeable Al^{3+} or Fe^{3+} by Ca^{2+} in the presence of B may result in precipitation of Al, Fe borates, or hydroxy borates (Biggar and Fireman 1960). Iron or aluminum, and boron seem to precipitate from solutions in stoichiometric proportions although the formation of discrete Fe or Al borates has not been demonstrated (Sims and Bingham 1968a). Boron $[\text{B}(\text{OH})_3]$ may be isostructural with $\text{Al}(\text{OH})_3$; fixation by layer lattice silicates has been observed (Couch and Grim 1968, Fleet 1965). For this reason, the B content of clay minerals has often been used as a paleosalinity indicator. Lengthy B adsorption kinetics (e.g., 20 to 100 hr for equilibration) further allude to the importance of precipitation and fixation reactions (Bingham et al. 1971, Griffin and Burau 1974).

Table 8-1. ADSORPTION CONSTANTS FOR BORON

Adsorbent						Adsorbate	Electrolyte			Adsorption Measurements		Reference
Identity (a)				CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (h)	Value (c)	
Soil	% Clay	% O.C.	% CaCO ₃									
25	1.00	0.80	16.2	59.8	-	CaCl ₂	0.01	6.02	A _m , K _L , C K _F , 1/N	0.729, 3.60, 0.466 1.93, 0.644	Eitrashidi and O'Connor 1982	
10	0.45	0.35	5.5	11.4	-	CaCl ₂	0.01	6.02	A _m , K _L , C K _F , 1/N	0.210, 3.44, 0.784 0.409, 0.666		
5.4	0.17	0.20	1.6	0.51	-	CaCl ₂	0.01	7.03	K _F , 1/N	0.087, 0.935		
5.0	0.02	8.40	6.2	11.2	-	CaCl ₂	0.01	8.00	K _F , 1/N	0.421, 1.19		
7.7	0.04	1.80	8.1	10.9	-	CaCl ₂	0.01	7.89	K _F , 1/N	0.162, 0.843		
5.6	0.04	8.00	7.8	14.6	-	CaCl ₂	0.01	7.82	A _m , K _L , C K _F , 1/N	0.408, 2.63, 2.13 0.125, 0.947		
57	0.97	8.80	35.2	177	-	CaCl ₂	0.01	7.57	A _m , K _L , C K _F , 1/N	3.13, 2.51, 1.45 3.99, 0.572		
27.3	1.10	20.2	18.5	65.9	-	CaCl ₂	0.01	7.62	A _m , K _L , C K _F , 1/N	1.50, 3.26, 1.30 2.53, 0.618		
13.7	0.43	0.5	14.0	64.9	-	CaCl ₂	0.01	7.42	A _m , K _L , C K _F , 1/N	1.07, 3.44, 0.407 2.16, 0.645		
Soil												
Yolo loam			17.8	109	10 ⁻⁴ - 10 ⁻²	-	-	8.0	A _m , K _L , C	1.22, 2.45, 1.94	Bigger and Fireman 1960	
Hesperia sand, loam			8.0	57	10 ⁻⁴ - 10 ⁻²	-	-	7.6	A _m , K _L , C	0.67, 3.00, 0.55		
Rincon loam			16.1	111	10 ⁻⁴ - 10 ⁻²	-	-	7.5	A _m , K _L , C	1.97, 2.77, 2.31		
Alken clay loam			19.9	12.0	10 ⁻⁴ - 10 ⁻²	-	-	1.7	A _m , K _L , C	4.40, 3.18, 0.55		

Table 8-1 (Contd). ADSORPTION CONSTANTS FOR BORON

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		Reference		
Identity (a)	CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)			
<u>Soils</u>											
10 Mexican and Hawaiian soils high in amorphous materials (10-40%)	-	-	10 ⁻³ - 10 ^{-2.2}	-	-	5.6- 6.0	A _m K _L	(26.4-53.0) (2.38 - 2.73)	Bingham et al. 1971		
<u>Soils</u>											
Terra Rosa	44.2	-	0 - 10 ^{-6.3} 0 - 10 ^{-6.3}	-	-	6.6	A _m , K _L "	2.96, 3.41 7.31, 3.07	Hadas and Hagin 1972		
K ⁺ saturated Terra Rosa	-	-	0 - 10 ^{-6.3} 0 - 10 ^{-6.3}	-	-	6.6	A _m , K _L "	3.98, 3.67 10.5, 3.30			
Grumusol	58.7	-	0 - 10 ^{-6.3} 0 - 10 ^{-6.3}	-	-	7.7	A _m , K _L "	5.09, 3.43 16.6, 2.23			
K ⁺ saturated Grumusol	-	-	0 - 120 ^{-5.5}	-	-	8.1	A _m , K _L	7.59, 3.25			
<u>Soil</u>	<u>% Clay</u>	<u>%O.C.</u>	<u>%CaCO₃</u>	<u>Soil</u>							
Loamy Sand	9.5	0.73	0	7.6	-	10 ⁻⁵ - 10 ⁻³	CaCl ₂	0.005	7.0	A _m , K _{HB} , K _B , K _{OH}	2.16, 2.34, 3.68, 5.04
Loam	21.7	0.68	18	17.0	-	10 ⁻⁵ - 10 ⁻³	CaCl ₂	0.005	7.7	A _m , K _{HB} , K _B , K _{OH}	2.91, 2.37, 4.21, 5.93
Clay	58.0	1.20	18	58.0	-	10 ⁻⁵ - 10 ⁻³	CaCl ₂	0.005	7.6	A _m , K _{HB} , K _B , K _{OH}	8.80, 2.35, 3.90, 5.31
Clay	65.2	0.24	0	31.0	-	10 ⁻⁵ - 10 ⁻³	CaCl ₂	0.005	7.0	A _m , K _{HB} , K _B , K _{OH}	14.10, 2.12, 3.90, 5.39

Table 8-1 (Contd). ADSORPTION CONSTANTS FOR BORON

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		Reference
Identity (a)	CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
Clay Minerals									
Kaolinite	-	39	10^{-4} - 10^{-2}	CaCl ₂	0.01	7.4	A _m , K _L	1.01, 4.67	
	-	-	-			9.9	" "	5.67, -	
Illite	-	130	10^{-4} - 10^{-2}	CaCl ₂	0.01	6.4	A _m , K _L	9.72, 3.23	Hingston 1964
						7.0	A _m , K _L	12.5, 3.23	
						6.5	A _m , K _L	14.3, 3.76	
						8.5	A _m , K _L	2.22, 3.81	
Montmorillonite	-	800	10^{-4} - 10^{-2}	CaCl ₂	0.01	7.5	A _m , K _L	1.52, 4.57	
						8.2	A _m , K _L	17.12, 3.41	
						9.4	A _m , K _L	50.9, 2.72	
Kaolinite (Ca-sat.)	-	-	10^{-4} - 10^{-2}	CaCl ₂	0.01	7-11	A _m , K _{HB} K _B , K _{OH}	0.272, 2.57, 4.24, 5.08	Keren and Mezuman 1981
Montmorillonite (Na-sat.)	-	-	10^{-4} - 10^{-3}	CaCl ₂	0.01	7-11	A _m , K _{HB} K _B , K _{OH}	0.55, 2.28, 3.24, 4.41	
Montmorillonite (Ca-sat.)	-	-	10^{-4} - 10^{-3}	CaCl ₂	0.01	7-11	A _m , K _{HB} K _B , K _{OH}	1.09, 2.02, 3.01, 3.96	
Illite (Ca-sat.)	-	-	10^{-4} - 10^{-3}	CaCl ₂	0.01	7-11	A _m , K _{HB} K _B , K _{OH}	1.39, 2.54, 3.94, 4.60	
Oahu 1	-	-	$10^{-3.3}$ - $10^{-2.3}$	-	-	-	A _m , K _L	(4.5, 5.4)	Okazaki and Chao 1968
2	-	-	$10^{-3.3}$ - $10^{-2.3}$	-	-	-	A _m , K _L	(3.1, 5.7)	
3	-	-	$10^{-3.3}$ - $10^{-2.3}$	-	-	-	A _m , K _L	(6.8, 5.5)	
4	-	-	$10^{-3.3}$ - $10^{-2.3}$	-	-	-	A _m , K _L	(4.0, 5.7)	
Maul 53	-	-	$10^{-3.3}$ - $10^{-2.3}$	-	-	-	A _m , K _L	(6.0, 5.5)	
Kauai 7	-	-	$10^{-3.3}$ - $10^{-2.3}$	-	-	-	A _m , K _L	(2.2, 6.1)	

Table 8-1 (Contd). ADSORPTION CONSTANTS FOR BORON

Adsorbent			Adsorbate		Electrolyte			Adsorption Measurements		Reference
Identify (a)	CEC meq/100g	S.A. m ² /g	Conc., M		Identity	Conc., M	pH	Constants (b)	Value (c)	
Soil										
Untreated										
sandy loams, acid	-	16.5	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	5.5	A _m , K _L	(0.3, 5.6)	Hatcher et al. 1967
	-	18.6	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	5.0	A _m , K _L	(0.3, 5.6)	
	-	19.4	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	4.7	A _m , K _L	(0.3, 5.9)	
	-	23.6	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	4.9	A _m , K _L	(0.3, 5.6)	
	-	31.0	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	5.8	A _m , K _L	(0.5, 5.7)	
sandy loams, calcareous	-	53.5	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	6.7	A _m , K _L	(1.2, 5.6)	
	-	66.9	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	7.4	A _m , K _L	(1.9, 5.7)	
	-	74.9	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	7.8	A _m , K _L	(2.8, 5.8)	
	-	83.7	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	7.7	A _m , K _L	(1.6, 5.6)	
	-	161.8	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	7.2	A _m , K _L	(2.7, 5.7)	
silt loams	-	93.9	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	8.3	A _m , K _L	(2.9, 5.7)	
	-	130.4	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	6.5	A _m , K _L	(2.5, 5.8)	
	-	292.0	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	7.6	A _m , K _L	(9.7, 5.5)	
clays, clay loams	-	117.4	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	7.4	A _m , K _L	(2.3, 5.8)	
	-	119.4	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	5.8	A _m , K _L	(5.1, 5.8)	
	-	249.1	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	7.4	A _m , K _L	(5.5, 5.7)	
	-	266.9	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	7.6	A _m , K _L	(4.0, 5.7)	
	-	295.2	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	7.7	A _m , K _L	(7.7, 5.2)	
subsoils	-	32.0	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	4.7	A _m , K _L	(0.5, 5.8)	
	-	38.6	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	4.6	A _m , K _L	(0.4, 5.9)	
	-	48.2	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	5.5	A _m , K _L	(0.6, 5.9)	
	-	64.6	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	5.3	A _m , K _L	(0.8, 5.9)	
	-	76.5	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	4.9	A _m , K _L	(1.2, 5.6)	
CaCO ₃ -treated										
sandy loams	-	8.0	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	7.4	A _m , K _L	(1.2, 5.2)	
	-	16.5	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	7.3	A _m , K _L	(0.6, 5.8)	
	-	18.6	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	7.4	A _m , K _L	(1.6, 5.5)	
	-	19.4	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	7.4	A _m , K _L	(3.6, 5.3)	
	-	23.6	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	7.5	A _m , K _L	(2.1, 5.5)	
	-	31.0	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	7.4	A _m , K _L	(1.3, 5.4)	
	-	35.0	10 ^{-3.3} - 10 ^{-2.7}	-	-	-	7.4	A _m , K _L	(1.9, 5.8)	

Table 8-1 (Contd). ADSORPTION CONSTANTS FOR BORON

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		Reference
Identity ^(a)	CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants ^(b)	Value ^(c)	
Soil						Soil			
clay, clay loams	-	119.4	10 ^{-3.3} - 10 ^{-2.7}	-	-	7.5	A _m , K _L	(7.4, 6.0)	
	-	127.0	10 ^{-3.3} - 10 ^{-2.7}	-	-	7.0	A _m , K _L	(10.2, 5.7)	
	-	161.0	10 ^{-3.3} - 10 ^{-2.7}	-	-	7.4	A _m , K _L	(7.0, 5.2)	
subsoils	-	32.2	10 ^{-3.3} - 10 ^{-2.7}	-	-	7.5	A _m , K _L	(1.8, 5.7)	
	-	38.6	10 ^{-3.3} - 10 ^{-2.7}	-	-	7.6	A _m , K _L	(2.1, 5.7)	
	-	48.2	10 ^{-3.3} - 10 ^{-2.7}	-	-	7.6	A _m , K _L	(1.7, 5.9)	
	-	64.6	10 ^{-3.3} - 10 ^{-2.7}	-	-	7.5	A _m , K _L	(3.2, 5.7)	
	-	76.3	10 ^{-3.3} - 10 ^{-2.7}	-	-	7.5	A _m , K _L	(4.0, 5.8)	
	-	121.4	10 ^{-3.3} - 10 ^{-2.7}	-	-	7.6	A _m , K _L	(3.5, 5.8)	

(a) O.C. = Organic carbon

(b) A_m = Langmuir adsorption maximum, $\mu\text{mol g}^{-1}$ K_L = Langmuir constant, $\log \text{M}^{-1}$ C = upper concentration limit for Langmuir equation, $\mu\text{mol ml}^{-1}$ $K_F, 1/N$ = Freundlich constants for $A = K_F C^{1/N}$; $A = \mu\text{mol g}^{-1}$; $C = \mu\text{M}$. K_{HB}, K_B, K_{OH} = competitive Langmuir constants for $B(OH)_3$, $B(ON)_4^-$, and OH^- , $\log \text{M}^{-1}$.

(c) () = estimated values.

Section 9

CADMIUM

The dominant cadmium (Cd) solution species in ground water at pH values < 8.2 and containing $< 10^{-2.5}$ M SO_4^{2-} activity is Cd^{2+} . Both precipitation/dissolution and adsorption/desorption reactions control Cd concentrations. Several researchers report that octavite (CdCO_3) limits Cd solution concentrations in alkaline soils. $\text{Cd}_3(\text{PO}_4)_2$ has also been reported to be a solubility-controlling solid. Although general adsorption mechanisms have been identified, detailed information is not available for making predictions of the environmental behavior of Cd. At low Cd concentrations ($< 10^{-5}$ M), Cd is specifically adsorbed by crystalline and amorphous oxides of Al, Fe, and Mn. At higher Cd concentrations ($> 10^{-5}$ M), nonspecific adsorption is the likely controlling mechanism. Metallic (Cu, Pb, Zn) and alkaline earth (Ca, Mg) cations reduce Cd adsorption by competition for available specific adsorption and cation exchange sites. The presence of ligands such as Cl^- and SO_4^{2-} may decrease Cd adsorption while $\text{S}_2\text{O}_3^{2-}$ has been shown to increase adsorption. These effects result from the relative stability of Cd-ligand versus Cd-surface complexes, the possible adsorption of Cd-ligand, and the effects of ligands on the charge distribution of the adsorptive surfaces.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIATION

Cadmium in aqueous solutions exists only in the +2 valence state. Lindsay (1979) calculated the relative stability of Cd compounds. His calculations show that at pH values < 7.5 most Cd compounds are more soluble than Cd levels found in soils (10^{-7} M). Under basic conditions, $\text{Cd}_3(\text{PO}_4)_2$ or CdCO_3 are likely to maintain Cd levels in soils.

To determine the relative abundance of Cd(II) species in ground waters representative of leachates, activities of different Cd species in equilibrium with $\text{Cd}^{+2} = 10^{-7}$ M or controlled by octavite were plotted (Figure 9-1) using the thermodynamic data (Ball et al. 1980) contained in the geochemical code MINTEQA (Felmy et al. 1983). Under the assumed conditions (Figure 9-1), Cd^{+2} followed by CdSO_4^0 is the dominant aqueous species in ground waters of pH values < 8.2 . At pH values > 8.2 ,

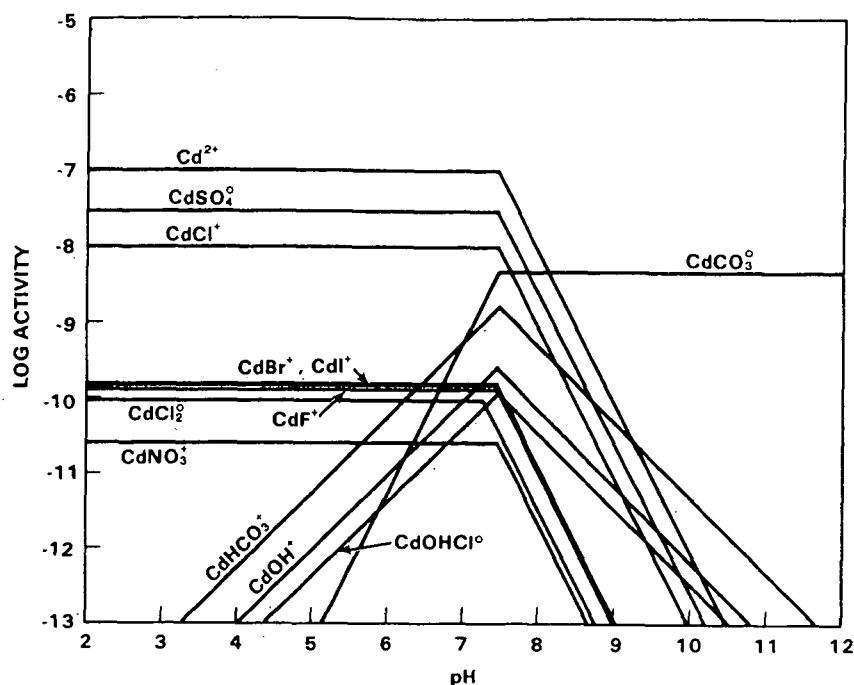


Figure 9-1. Activity of different cadmium species when $\text{Cd}^{2+} = 10^{-7}$ or controlled by octavite (CdCO_3) and when $\text{SO}_4^{2-} = \text{Cl}^- = 10^{-3}$, $\text{NO}_3^- = \text{F}^- = 10^{-4}$, $\text{Br}^- = \text{I}^- = 10^{-5}$ and $\text{CO}_2(\text{gas}) = 10^{-3.52}$ atmospheres.

CdCO_3^0 species are dominant. With the exception of CdCl^+ which contributes approximately 10% to the total Cd at pH values < 8.2 , other Cd complexes with Br^- , F^- , NO_3^- , I^- , and OH^- do not contribute significantly to the total Cd in solution.

PRECIPITATION/DISSOLUTION

Several studies show that CdCO_3 limits Cd solution concentrations in alkaline soils ($\text{pH} > 7$). Cavallaro and McBride (1978) and McBride (1980) clearly demonstrate that $\text{CdCO}_3(\text{s})$ precipitates in calcareous soils ($\text{pH} > 7.8$) even though adsorption reactions predominate in soils of neutral or acidic pH. Street et al. (1977, 1978) based on solubility measurements of Cd in alkaline soils, showed that Cd concentrations were limited by the solubility of CdCO_3 . Jenne et al. (1980) working with the waters associated with abandoned Pb and Zn mines and tailings piles, also indicate that the upper limits on dissolved levels of Cd in most waters were controlled by CdCO_3 . Levi-Minzi et al. (1976) observed that the interaction of Cd^{2+} with calcareous soils was not adequately explained by physical adsorption alone. Although Levi-Minzi

et al. (1976) were unable to identify a Cd-solid phase which precipitated, they were able to demonstrate that chemical interaction was occurring.

Santillan-Medrano and Jurinak (1975) observed that activity of Cd in Cd-amended soils was lowest in calcareous soils. At higher concentrations ($>5 \times 10^{-6}$ M), $\text{Cd}_3(\text{PO}_4)_2$ or CdCO_3 were observed to control Cd concentrations. Street et al. (1977) suggest that CdCO_3 and $\text{Cd}_3(\text{PO}_4)_2$ most likely limit Cd^{2+} activities in soils.

Frost and Griffin (1977b) suggested that precipitation may be responsible for the removal of Cd from landfill leachates when $\text{pH} > 6$. Baes and Mesmer (1976) suggested that $(\text{Ca-Cd})\text{CO}_3$ solid solutions are expected and may be an important mechanism in controlling Cd concentrations in calcareous soils.

ADSORPTION/DESORPTION

In contrast to other transition series metals, the adsorption of Cd (Table 9-1) often correlates with the cation exchange capacity (CEC) of the soil (John 1971; Levi-Minzi et al. 1976; Navrot et al. 1978; Petruzelli et al. 1978; Sidle and Kardos 1977; Singh 1979; McBride et al. 1981). At low solution concentration of Cd, adsorption correlates with exchangeable Ca, Al, or Zn (John 1971; John 1972; McBride et al. 1981), a further indication of an ion exchange mechanism. Although organic matter may influence adsorption of Cd by soils and sediments (John 1971; Levi-Minzi et al. 1976; Sidle and Kardos 1977; Singh and Sekhon 1977a), this effect is probably due to the CEC of the organic material rather than to complexation by organic ligands (Singh and Sekhon 1977a). In fact, removal of organic material from soils does not markedly reduce Cd adsorption and, in some cases, may enhance adsorption (Petruzelli et al. 1978). The adsorption of Cd by soil or subsoil materials may, to a large degree, be an exchange reaction with Ca or Mg. However, Cd appears to be selected over Ca (Milberg et al. 1978). Specific adsorption to calcite (McBride 1980) and hydrous oxides of Al and Fe (Kinniburgh et al. 1977; Forbes et al. 1976; Benjamin and Leckie 1981) does occur and may be the most important adsorption mechanism at low environmental concentrations of Cd.

As with other cationic metals, Cd adsorption exhibits pH dependency (Table 9-1). The effect of pH on Cd adsorption by soils (Huang et al. 1977), sediments (Reid and McDuffie 1981), clay minerals (Farrah and Pickering 1977; Frost and Griffin 1977b), alumina (Kinniburgh et al. 1977; Kinniburgh et al. 1976; Benjamin and Leckie 1980a), silica (Schindler et al. 1976; Stumm et al. 1976; Benjamin and Leckie 1980), and Fe oxides (Balistrieri and Murray 1982, Forbes et al. 1976, Gadde and Laitinen 1974, Kinniburgh et al. 1977) is influenced by the solution:solid ratio, the solution

concentration of Cd, and the presence of competing cations or complexing ligands. At low Cd solution concentrations, sharp adsorption gradients as a function of pH indicate that specific adsorption (i.e., surface complexation), occurs. Under comparable experimental conditions, the adsorption edge falls at higher pH than that of Pb, Cu, and Zn. This order is consistent with the pH of hydrolysis of metals. At higher Cd concentrations or in the presence of competing cations such as Mg, the adsorption edge is less defined and nonspecific adsorption or exchange is likely the controlling mechanism.

Competition between cations for adsorption sites strongly influences the adsorption behavior of Cd (Table 9-1). The presence of Ca, Mg, and trace metal cations reduces the adsorption of Cd by soils (Cavallaro and McBride 1978; Singh 1979), clay minerals (Stuanes 1976; Bittell and Miller 1974; Farrah and Pickering 1977), Fe oxides (Balistrieri and Murray 1982; Benjamin and Leckie 1980); Mn oxides (Gadde and Laitinen 1974); and alumina (Benjamin and Leckie 1980). The extent of competition between Cd and other ions depends on the relative energies of interaction between the ions and the adsorbing surface, the concentrations of the competing ions, and solution pH.

The relative stability of Cd-ligand versus Cd-surface complexes, the possible adsorption of Cd-ligand solution complexes, and the effect of ligands on the electrostatic conditions at the solution/solid interface are factors influencing the adsorptive behavior of Cd. The adsorption of Cd by clay minerals (Garcia-Miragaya and Page 1976; Egozy 1980), lepidocrocite (α -FeOOH), amorphous $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, silica, or alumina (Benjamin and Leckie 1980) is reduced by the presence of chloride (Table 9-1). In contrast, the adsorption of Cd by goethite (α -FeOOH) is not significantly affected by chloride concentrations exceeding 0.5 M (Balistrieri and Murray 1982). Sulfate reduces Cd adsorption by amorphous $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Benjamin and Leckie 1982). Thiosulfate, however, increases Cd adsorption. The increased adsorption, especially below pH 7, is consistent with the adsorption behavior of free S_2O_3 on these surfaces and implies binding of Cd-thiosulfate complexes. The addition of EDTA inhibited the adsorption of Cd by $\text{Al}(\text{OH})_3$, and $\text{Fe}(\text{OH})_3$, and clay minerals at all pH values (Chubin and Street 1981). Extracts of water soluble constituents from sewage sludge and organic soil enhance Cd adsorption at higher pH and reduce it at low pH (Chubin and Street 1981).

The soil organic fraction does not demonstrate marked affinity for Cd (Table 9-1). Clay minerals with adsorbed humic acids (organo-clay complexes) do not adsorb Cd in excess of the clay minerals alone; clay minerals, however, coated with Fe or Al

oxides are considerably more effective (Levy and Francis 1976). The adsorption of Cd by clay-humic acid mixtures is equivalent to the sum of the uptake by individual adsorbents (Hatton and Pickering 1980).

At low Cd solution concentration, Cd is specifically adsorbed through surface complexation of Cd^{2+} and CdOH^+ by amphoteric surface hydroxyl sites (Davis and Leckie 1978; Balistrieri and Murray 1982). Oxides of Fe have a strong specific adsorption capacity for Cd. When surface coverage is high, Cd retention in soil and sediment is controlled by ion exchange (Navrot et al. 1978; McBride et al. 1982) in which Cd^{2+} competes with exchangeable Ca^{2+} and Mg^{2+} . The ionic radius of Cd^{2+} is comparable to that of Ca^{2+} and rapid exchange of the two elements may occur.

The specific adsorption of Cd by soil appears to occur at select limited binding sites on Al_2O_3 , FeOOH , and $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{am})^*$ (Levy and Francis 1976; Benjamin and Leckie 1980) or on edge sites of layer lattice silicates (Levy and Francis 1976). The addition of Cu or Pb, which are more strongly adsorbed, slightly reduces Cd adsorption by Al_2O_3 and FeOOH suggesting that Cu and Pb are preferentially adsorbed by different surface sites (Benjamin and Leckie 1980). In contrast, Zn almost completely displaces Cd, indicating that Cd and Zn compete for the same group of binding sites. On iron oxyhydroxide, Cd, Cu, Zn and Pb each adsorb preferentially to different surface sites (Benjamin and Leckie 1980).

*Fe-oxides may exist as coatings on clay-sized minerals (Jenne 1977).

Table 9-1. ADSORPTION CONSTANTS FOR CADMIUM

Adsorbent		Adsorbate		Electrolyte			Adsorption Measurements		Reference
Identified ^(a)	CEC meq/100g	S.A. m ² /g	Conc., M	Identify	Conc., M	pH	Constants ^(b)	Value ^(c)	
<u>Clay Minerals</u>									
Montmorillonite, Na-form	-	-	$10^{-6.9} - 10^{-6}$	-	-	6.5- 7.0	$K_F, 1/N, a,$ b, A_m, K_L	5.68, 0.69, 0.06 16.93, (0.7, 7.8)	Garcia-Miragaya and Page 1976
						6.5- 7.0	"	4.98, 0.74, 0.05, 10.46, (0.5, 7.7)	
						6.5- 7.0	"	1.81, 0.74, 0.05, 2.76, (0.4, 7.2)	
						6.5- 7.0	"	0.86, 0.86, 0.02 0.93, (0.4, 6.8)	
						6.5- 7.0	"	0.51, 0.76, 0.03, 0.55, (0.2, 6.9)	
						6.5- 7.0	"	0.31, 0.51, 0.07 0.28, (0.3, 6.7)	
				NaCl	0.01	6.5- 7.0	"	44.56, 1.57, -0.12, 10.46, (-, -)	
						6.5- 7.0	"	0.43, 0.79, 0.02, 0.44, (0.4, 6.3)	
						6.5- 7.0	"	0.34, 0.89, 0.0, 0.41, (0.3, 6.3)	
						6.5- 7.0	"	0.16, 1.01, -0.01, 0.16, (0.1, 6.7)	
						6.5- 7.0	"	0.09, 1.26, -0.01, 0.10, (0.2, 5.6)	

Table 9-1 (Contd). ADSORPTION CONSTANTS FOR CADMIUM

Adsorbent			Adsorbate		Electrolyte			Adsorption Measurements		Reference
Identified ^(a)	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identify	Conc., M	pH	Constants ^(b)	Value ^(c)		
Clay Minerals (contd)										
Montmorillonite, Na-form	-	-	10 ^{-6.9} - 10 ⁻⁶	Na ₂ SO ₄	0.03	6.5- 7.0	K _F , 1/N, a b, A _m , K _L	3.90, 1.03, 0.00 3.64, (0.9, 6.7)	Garcia-Miragaya and Page 1976	
					0.05	6.5- 7.0	"	0.74, 0.78, 0.03 0.85, (0.8, 6.3)		
					0.075	6.5- 7.0	"	0.63, 0.82, 0.04, 0.63, (0.7, 6.2)		
Bentonite	-	-	0 - 10 ^{-4.7}	Seawater	~0.7	8.0	A _m , K ^L	(1.2, 6.2)		
Montmorillonite Na-form	-	-		NaCl +					Egozy 1980	
			10 ^{-2.2}	NaOAc	0.1, 0.1	5.2	A, K _d	10, (1.5)		
			10 ^{-3.1}		0.1, 0.1	6.4	A, K _d	10, (12)		
			10 ^{-3.5}		0.1, 0.1	5.2	A, K _d	1, (3.3)		
			10 ^{-4.6}		0.1, 0.1	6.4	A, K _d	1, (37)		
			10 ^{-4.8}		0.1, 0.1	5.2	A, K _d	0.1, (6)		
			10 ^{-6.0}		0.1, 0.1	6.4	A, K _d	0.1, (90)		
			10 ⁻⁶ - 10 ⁻⁷	NaNO ₃ +	1.0, 0.01	5.0	K _d	(8)		
				NaOAc	1.0, 0.01	6.5	K _d	(100)		
					0.1, 0.01	5.0	K _d	(40)		
					0.1, 0.01	6.5	K _d	(270)		
			10 ⁻⁶ - 10 ⁻⁷	NaNO ₃ +	0.01, 0.01	5.0	K _d	(210)		
				NaOAc	0.01, 0.01	6.5	K _d	(900)		
				NaCl +	1.0, 0.01	5.0	K _d	(<0.5)		
				NaOAc	1.0, 0.01	6.5	K _d	(1.5)		
					0.1, 0.01	5.0	K _d	(9)		
					0.1, 0.01	6.5	K _d	(100)		
					0.01, 0.01	5.0	K _d	(130)		
					0.01, 0.01	6.5	K _d	(900)		
Montmorillonite, Na-form	-	-	Trace ¹⁰⁹ Cd	Ca(NO ₃) ₂	0.01	-	K _d	59		Levy and Francis 1976
+ H.A., (a) 3.3 mgC g ⁻¹	-	-	Trace ¹⁰⁹ Cd	Ca(NO ₃) ₂	0.01	-	K _d	56		
Ca-form	-	-	Trace ¹⁰⁹ Cd	Ca(NO ₃) ₂	0.01	-	K _d	104		
+ H.A., 6.4 mgC g ⁻¹	-	-	Trace ¹⁰⁹ Cd	Ca(NO ₃) ₂	0.01	-	K _d	89		
Al-form	-	-	Trace ¹⁰⁹ Cd	Ca(NO ₃) ₂	0.01	-	K _d	33		
+ H.A., 12.5 mgC g ⁻¹	-	-	Trace ¹⁰⁹ Cd	Ca(NO ₃) ₂	0.01	-	K _d	52		
Fe-form	-	-	Trace ¹⁰⁹ Cd	Ca(NO ₃) ₂	0.01	-	K _d	43		
+ H.A., 14.3 mgC g ⁻¹	-	-	Trace ¹⁰⁹ Cd	Ca(NO ₃) ₂	0.01	-	K _d	61		

(a) Humic acid

Table 9-1 (Contd). ADSORPTION CONSTANTS FOR CADMIUM

Adsorbent			Adsorbate		Electrolyte			Adsorption Measurements		Reference
Identified (a)	CEC meg/100g	S ₂ A. m ² /g	Conc., M	Identify	Conc., M	pH	Constants (b)	Value (c)		
<u>Clay Minerals</u>										
Montmorillonite,	-	-	Trace ¹⁰⁹ Cd	Ca(NO ₃) ₂	0.01	-	K _d	614	Levy and Francis 1976	
Al(OH) ₃ -coated	-	-	Trace ¹⁰⁹ Cd	Ca(NO ₃) ₂	0.01	-	K _d	376		
+ H.A., 3.3 mgC g ⁻¹	-	-								
	-	-								
Fe(OH) ₃ -coated	-	-	Trace ¹⁰⁹ Cd	Ca(NO ₃) ₂	0.01	-	K _d	222		
+ H.A., 2.0 mg L g ⁻¹	-	-	Trace ¹⁰⁹ Cd	Ca(NO ₃) ₂	0.01	-	K _d	150		
Montmorillonite	70	-	0.0005 - 0.05	ΣCl ⁻	0.01 - 0.1	5-6	A _m , K _L	(310, 2.9)	Stuanes 1976	
			0.025 - 0.075	ΣCl ⁻	0.1	5-6	K _{Cd} ^{Zn}	2.0-2.25		
			0.0025 - 0.0075	ΣCl ⁻	0.01	5-6		1.62-1.70		
			0.025 - 0.075	ΣCl ⁻	0.1	5-6	K _{Cd} ^{Mn}	1.75-2.08		
			0.0025 - 0.0075	ΣCl ⁻	0.01	5-6		1.33-1.54		
			0.00025 - 0.075	ΣCl ⁻	0.01, 0.1	5-6	K _{Hg} ^{Cd}	99-∞		
Kaolinite	4	-	0.005 - 0.05	ΣCl ⁻	0.01 - 0.1	5-6	A _m , K _L	(16, 2.8)		
			0.0025 - 0.075	ΣCl ⁻	0.01, 0.1	5-6	K _{Cd} ^{Zn}	1.25-1.54		
			0.025 - 0.75	ΣCl ⁻	0.1	5-6	K _{Cd} ^{Mn}	1.25-1.34		
			0.0025 - 0.0075	ΣCl ⁻	0.01	5-6		1.38-1.51		
			0.025 - 0.075	ΣCl ⁻	0.1	5-6	K _{Hg} ^{Cd}	10.5-19.7		
			0.0025 - 0.0075	ΣCl ⁻	0.01	5-6		10.5-27.0		
Vermiculite	70		0.005 - 0.05	ΣCl ⁻	0.01 - 0.1	5-6	A _m , K _L	(440, 2.7)		
			0.025 - 0.075	ΣCl ⁻	0.1	5-6	K _{Cd} ^{Zn}	3.83-5.54		
			0.0025 - 0.0075	ΣCl ⁻	0.01	5-6		4.38-5.82		
			0.025 - 0.075	ΣCl ⁻	0.1	5-6	K _{Cd} ^{Mn}	1.33-1.61		
			0.0025 - 0.0075	ΣCl ⁻	0.01	5-6		1.22-1.25		
			0.0025 - 0.075	ΣCl ⁻	0.01, 0.1	5-6	K _{Hg} ^{Cd}	99-∞		

Table 9-1 (Contd). ADSORPTION CONSTANTS FOR CADMIUM

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		Reference
Identified (a)	CEC meq/100g	S ₂ A _s m ² /g	Conc., M	Identify	Conc., M	pH	Constants (b)	Value (c)	
Clay Minerals									
Montmorillonite	96	-	0.005 - 0.05	ΣCl ⁻	0.01 - 0.1	5-6	A _m , K _L	(460, 2.6)	Stuanes 1976
Feldspars:									
Albite	-	-	0.005 - 0.05	ΣCl ⁻	0.01 - 0.1	5-6	A _m , K _L	(2.9, 1.9)	
Montmorillonite	106	-	-			4.8-	K ^{Ca} _{Cd}		Bittell and Miller 1974
Ca-saturated		-		Σ salts	10 ⁻³	6.5		1.2	
Cd-saturated		-		Σ salts	10 ⁻³			0.87	
Pb-saturated		-		Σ salts	10 ⁻³	4.8-	K ^{Cd} _{Pb}	0.44	
Cd-saturated		-		Σ salts	10 ⁻³	6.5		0.72	
Illite,	15.4	-	-			4.8-	K ^{Ca} _{Cd}		Bittell and Miller 1974
Ca-saturated		-		Σ salts	10 ⁻³	6.5		0.79	
Cd-saturated		-		Σ salts	10 ⁻³			1.2	
Pb-saturated		-		Σ salts	10 ⁻³	4.8-	K ^{Cd} _{Pb}	0.47	
Cd-saturated		-		Σ salts	10 ⁻³	6.5		0.65	
Kaolinite,	22	-	-			4.8-	K ^{Ca} _{Cd}		Bittell and Miller 1974
Ca-saturated		-		Σ salts	10 ⁻³	6.5		0.85	
Cd-saturated		-		Σ salts	10 ⁻³			0.94	
Pb-saturated		-		Σ salts	10 ⁻³	4.8-	K ^{Cd} _{Pb}	0.28	
Cd-saturated		-		Σ salts	10 ⁻³	6.5		0.34	

Table 9-1 (Contd). ADSORPTION CONSTANTS FOR CADMIUM

Adsorbent			Adsorbate		Electrolyte			Adsorption Measurements		Reference
identified (a)	CEC meq/100g	S ₂ A _s m/g	Conc., M	Identify	Conc., M	pH	Constants (b)	Value (c)		
<u>Fe Oxides (contd)</u>										
Amorphous Fe(OH) ₃	-	-	0 - 10 ^{-5.2}	Seawater	~0.7	8	A _m , K _L	(4.9, 6.2)	Oakley et al. 1981	
Amorphous Fe ₂ O ₃ ·H ₂ O	-	-	0 - 10 ^{-7.7}	NaNO ₃	0.1	6.8	K _F , 1/N	(1.1, 1.0)	Benjamin and Leckie 1981	
			10 ^{-7.7} - 10 ⁻⁴	"	"	6.6	"	(0.065, 0.67)		
			"	"	"	6.9	"	(0.15, 0.67)		
			"	"	"	7.2	"	(0.32, 0.67)		
Amorphous Fe ₂ O ₃ ·H ₂ O -Cocprecipitation			10 ^{-6.1}	KNO ₃	10 ⁻²	8.5	K _d	180	Bruninx 1975	
				Synthetic river water	-	-		80		
<u>Mn Oxides</u>				Synthetic seawater	~0.7	8.5	K _d	3.7		
Hydrous MnO ₂	-	-	10 ⁻⁴ - 10 ^{-2.5}	-	-	6	A _m , K _L	(2000, 4.0)	Gadd and Laitonen 1974	
Hydrous MnO ₂	-	-	0 - 10 ^{-3.5}	Seawater	~0.7	8	"	(17, 6.3)		
<u>Ti Oxides</u>										
TiO ₂	-	-	10 ^{-3.7}	-	-	-	K _{Cd} ^{Int}	7.2, 10.1	Davis and Leckie 1978	
							K _{CdOH} ^{Int}			
TiO ₂	-	-	-	NaClO ₄	1.0	-	*KTiOCd, *R(TiO) ₂ Cd	-3.2, -10.5	Stumm et al. 1976	
<u>Calcite</u>										
Fine	-	0.49	10 ^{-5.6} - 10 ⁻³	-	-	6-9	A _m	32	McBride 1980	
Coarse	-	0.22	10 ^{-5.6} - 10 ⁻³	-	-	6.9	A _m	3.5		
<u>Organic Material</u>										
Soil humic acids	-	-	10 ⁻³ - 10 ^{-2.4}	-	-	5.8	A _m , K _L	56.0, 2.6	Riffaldi and Levi-Minzi 1975	
	-	-	10 ⁻³ - 10 ^{-2.4}	-	-	5.8	"	93.6, 3.2		
	-	-	10 ⁻³ - 10 ^{-2.4}	-	-	5.8	"	86.6, 3.1		
Peat	120	-	10 ^{-4.6} - 10 ^{-3.6}	-	-	~4	A _m , K _L	(190, 5.0)	Bunzl et al. 1976	
Humic acid	-	-	0 - 10 ^{-3.2}	Seawater	~0.7	8	A _m , K _L	(5.6, 5.0)	Oakley et al. 1981	

Table 9-1 (Contd). ADSORPTION CONSTANTS FOR CADMIUM

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		Reference
Identified ^(a)	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identify	Conc., M	pH	Constants ^(b)	Value ^(c)	
<u>Clay Minerals</u>									
SiO ₂	-	160		NaClO ₄	1.0	6-8	*K ₁ ^S (Si-OCd)	-6.09	Schindler et al. 1976
							*K ₂ ^S ((SiO) ₂ Cd)	-14.20	
							K _{Cd} ^{Int} , K _{CdOH} ^{Int}	(1.1, 3.1)	Stumm et al. 1976
α-SiO ₂	-	-	10 ^{-6.3}	-	-	-	K _{Cd} ^{Int} , K _{CdOH} ^{Int}	-, 5.0	Davis and Leckie 1978
<u>Alumina</u>									
α-Al ₂ O ₃	-	-	10 ^{-6.3}	-	-	-	K _{Cd} ^{Int} , K _{CdOH} ^{Int}	5.9, 9.7	Davis and Leckie 1978
<u>Fe-Oxides</u>									
α-FeOOH (goethite)	-	-	10 ^{-3.7}	-	-	-	K _{Cd} ^{Int} , K _{CdOH} ^{Int}	6.0, 9.3	Davis and Leckie 1978
α-FeOOH	-	-	10 ^{-3.6}	Seawater	~0.7	-	*K _{Cd} ^{Int} , *K _{CdOH} ^{Int}	(9.1, 11.2)	
α-FeOOH	-	-	-	-	-	-	K _c ^I	-3.8	Forbes et al. 1976
Amorphous Fe ₂ O ₃ ·H ₂ O			10 ^{-6.3}	-	-	-	K _{Cd} ^{Int} , K _{CdOH} ^{Int}	5.8, 9.8	Davis and Leckie 1978

Table 9-1 (Contd). ADSORPTION CONSTANTS FOR CADMIUM

Adsorbent			Adsorbate		Electrolyte		Adsorption Measurements		Reference
Identified (a)	CEC meq/100g	S ₂ A ₂ m ² /g	Conc., M	Identify	Conc., M	pH	Constants (b)	Value (c)	
<u>Soil</u>									
Lansing A	6.6	-	10 ⁻⁵ - 10 ^{-3.5} 10 ⁻⁵ - 10 ^{-3.5}	- CaCl ₂	- 0.01	- 6.3 6.3	A _m , K _L	20, 5.2 1.0, 4.3	Cavallaro and McBride 1978
C	9.5	-	10 ⁻⁵ - 10 ^{-3.5}	-	-	8.4	A _m , K _L	20, 5.1	
Mardin A	5.5	-	10 ⁻⁵ - 10 ^{-3.5} 10 ⁻⁵ - 10 ^{-3.5}	- CaCl ₂	- 0.01	4.7 4.7	A _m , K _L	6, 5.3 0, -	
30 Soils - composite	-	-	10 ^{-4.4} - 10 ^{-3.1}	-	-	-	A _m , K _L	44, 4.9	John 1971
5 Organic soils	-	-	10 ^{-5.1} - 10 ^{-3.1}	-	-	-	"	46 ± 6; 5.2 ± 0.2	John 1972
8 Heavy clays	-	-	"	-	-	-	"	43 ± 3; 5.0 ± 0.2	
12 Sandy and silt loams	-	-	"	-	-	-	"	44 ± 6; 5.0 ± 0.3	
5 Sandy soils	-	-	"	-	-	-	"	44 ± 3; 4.8 ± 0.3	
All soils	-	-	"	-	-	-	"	44 ± 5; 5.0 ± 0.3	
<u>Soil % Clay % O.M.</u>									
7.0	7.8	32.5	-	10 ^{-3.4} - 10 ^{-2.9}	-	-	<u>Soil</u> 7.7 A _m , K _L	90, 4.4	Levi-Minzi et al. 1976
16.1	2.7	27.5					7.9 A _m , K _L	78, 3.9	
4.0	0.9	8.8					8.2 A _m , K _L	27, 3.8	
6.8	4.2	20.0					7.9 A _m , K _L	69, 4.3	
1.8	1.7	15.0					8.1 A _m , K _L	38, 4.2	
34.7	1.0	20.0					8.6 A _m , K _L	68, 3.8	
10.9	3.1	17.5					8.5 A _m , K _L	47, 4.2	
7.7	2.1	16.2					8.3 A _m , K _L	40, 4.2	
24.9	4.5	31.2					8.1 A _m , K _L	94, 4.4	
14.9	4.2	30.0					7.7 A _m , K _L	89, 4.1	
<u>% O.C.</u>									
0.21	8.2	65	0 - 10 ^{-2.4}	NaCl	0.01		<u>Soil</u> 8.2 A _m , K _L	42, 3.8	Navrot et al. 1978
0.83	15.4	85	0 - 10 ^{-2.4}	NaCl	0.01		7.8 A _m , K _L	53, 4.4	
0.23	18.9	131	0 - 10 ^{-2.4}	NaCl	0.01		8.3 A _m , K _L	57, -	
0.79	31.8	226	0 - 10 ^{-2.4}	NaCl	0.01		7.6 A _m , K _L	62, 4.0	
0.86	37.0	315	0 - 10 ^{-2.4}	NaCl	0.01		7.9 A _m , K _L	89, 3.6	

Table 9-1 (Contd). ADSORPTION CONSTANTS FOR CADMIUM

Adsorbent				Adsorbate		Electrolyte		Adsorption Measurements			Reference
Identified (a)			CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identify	Conc., M	pH	Constants (b)	Value (c)	
Soil	% Clay	% O.M.									
	59.6	21.6	57.5	-	0 - 10 ^{-2.9}	-	-		Soil		
	59.6	0	23.7	-	0 - 10 ^{-2.9}	-	-		5.4 A _m , K _L	62, 4.2	Petrucelli et al. 1978
									5.4 A _m , K _L	75, 3.9	
Cu-enriched soil											
	59.6	21.6	-	-	0 - 10 ^{-2.9}	-	-	-	A _m , K _L	45, 3.0	
	36.3	3.3	38.8	-	0 - 10 ^{-2.9}	-	-	6.7	A _m , K _L	54, 4.4	
	36.3	0	11.3	-	0 - 10 ^{-2.9}	-	-	6.7	A _m , K _L	34, 3.7	
	12.9	17.8	22.6	-	0 - 10 ^{-2.9}	-	-	7.0	A _m , K _L	109, 4.8	
	12.9	0	15.4	-	0 - 10 ^{-2.9}	-	-	7.0	A _m , K _L	54, 4.4	
	18.9	3.5	27.5	-	0 - 10 ^{-2.9}	-	-	6.0	A _m , K _L	36, 4.1	
	18.9	0	13.1	-	0 - 10 ^{-2.9}	-	-	6.0	A _m , K _L	46, 3.7	
Depth % O.M.											
0-7.5 cm		10.6	18.4	-	10 ^{-7.4} - 10 ^{-5.8}	simulated	-	7.2	A _m , K _L	0.021, 6.7,	Sidle and Kardos 1977
						sludge			K _F , 1/N	0.048, 0.82	
7.5-15 cm		5.4	8.4	-	10 ^{-7.4} - 10 ^{-5.8}	leachate		7.2	"	0.013, 6.5, 0.014, 0.71	
% Clay % O.C.											
	10.1	0.61	6.96	-	10 ^{-4.4} - 10 ^{-3.1}	KCl	0.1	7.0	A _m , K _L	7.5, 3.3	Singh and Sekhon 1977
	31.2	1.26	18.23	-	10 ^{-4.4} - 10 ^{-3.1}	KCl	0.1	7.0	A _m , K _L	22, 4.0	
	10.4	0.69	6.09	-	10 ^{-4.4} - 10 ^{-3.1}	KCl	0.1	7.0	A _m , K _L	8.5, 3.3	
	24.6	0.75	12.18	-	10 ^{-4.4} - 10 ^{-3.1}	KCl	0.1	7.0	A _m , K _L	12.5, 3.5	
	20.2	0.76	10.44	-	10 ^{-4.4} - 10 ^{-3.1}	KCl	0.1	7.0	A _m , K _L	8.5, 3.4	
	5.5	0.33	3.83	-	10 ^{-4.4} - 10 ^{-3.1}	KCl	0.1	7.0	A _m , K _L	6.5, 3.3	
	8.9	0.34	4.35	-	10 ^{-4.4} - 10 ^{-3.1}	KCl	0.1	7.0	A _m , K _L	7.0, 3.3	
% O.C.											
	3.98		9.01	-	10 ^{-3.2} - 10 ^{-4.2}	-	-		Soil		Singh 1979
	3.98		9.01	-	10 ⁻⁷ - 10 ^{-5.7}	-	-		4.8 A _m , K _L	(40, 7.5)	
	1.66	1.22	-	-	10 ⁻⁷ - 10 ^{-5.7}	-	-		4.8 A _m , K _L	(4.7, 6.2)	
	1.72	3.58	-	-	10 ⁻⁷ - 10 ^{-5.7}	-	-		4.3 A _m , K _L	(0.6, 5.7)	
	2.95	7.55	-	-	10 ⁻⁷ - 10 ^{-5.7}	-	-		4.3 A _m , K _L	(1.6, 5.9)	
	4.23	6.98	-	-	10 ⁻⁷ - 10 ^{-5.7}	-	-		3.9 A _m , K _L	(1.4, 5.8)	
	2.47	16.51	-	-	10 ⁻⁷ - 10 ^{-5.7}	-	-		3.6 A _m , K _L	(1.2, 6.2)	
	6.14	13.05	-	-	10 ⁻⁷ - 10 ^{-5.7}	-	-		4.6 A _m , K _L	(3.0, 5.8)	
	1.47	5.24	-	-	10 ⁻⁷ - 10 ^{-5.7}	-	-		4.3 A _m , K _L	(3.9, 6.0)	
	2.24	11.81	-	-	10 ⁻⁷ - 10 ^{-5.7}	-	-		4.3 A _m , K _L	(2.7, 6.2)	
			-	-	10 ⁻⁷ - 10 ^{-5.7}	-	-		4.8 A _m , K _L	(2.6, 5.8)	
	0.61	3.24	-	-	10 ⁻⁷ - 10 ^{-5.7}	-	-		4.2 A _m , K _L	(1.4, 7.1)	

Table 9-1 (Contd). ADSORPTION CONSTANTS FOR CADMIUM

Adsorbent			Adsorbate		Electrolyte		Adsorption Measurements			Reference
Identified (a)	CEC meg/100g	S ₂ A. m ² /g	Conc., M		Identify	Conc., M	pH	Constants (b)	Value (c)	
Soil	% O.M.									
	0.72	60.0	-	10 ^{-6.9} - 10 ^{-5.9}	-	-		Soil		
							8.4	K _F , 1/N,	23.2, 0.72	Garcia-Miragaya 1980
							a, b	0.20, 54.3		
	16.3	33.8	-	10 ^{-6.9} - 10 ^{-5.9}			5.2	K _F , 1/N,	6.8, 0.66,	
							a, b	0.16, 16.0		
	1.8	25.0	-	10 ^{-6.9} - 10 ^{-5.9}			6.0	K _F , 1/N,	8.3, 0.95,	
							a, b	0.0, 9.7		
	1.5	23.8	-	10 ^{-6.9} - 10 ^{-5.9}			5.8	K _F , 1/N,	3.6, 0.63,	
							a, b	0.03, 15.5		
% Clay	% O.M.							Soil		
10	1.79	4.7	-	10 ⁻⁵	-	-	4.8	K _{rc}	2.5	McBride et al. 1981
29	0.12	5.1	-	10 ⁻⁵	-	-	4.5	"	0.8	
5	1.31	3.9	-	10 ⁻⁵	-	-	4.8	"	1.0	
15	0.36	6.1	-	10 ⁻⁵	-	-	5.0	"	2.3	
2	1.15	2.2	-	10 ⁻⁵	-	-	5.0	"	0.7	
3	0.15	1.2	-	10 ⁻⁵	-	-	5.2	"	0.7	
9	7.33	23.2	-	10 ⁻⁵	-	-	6.0	"	13.5	
20	2.90	11.1	-	10 ⁻⁵	-	-	6.0	"	6.0	
15	2.43	11.2	-	10 ⁻⁵	-	-	6.8	"	13.5	
21	1.02	10.3	-	10 ⁻⁵	-	-	7.3	"	10.5	
15	2.91	11.5	-	10 ⁻⁵	-	-	5.2	"	4.1	
14	1.22	8.4	-	10 ⁻⁵	-	-	5.0	"	2.4	
17	2.50	14.9	-	10 ⁻⁵	-	-	5.7	"	6.5	
19	0.88	18.2	-	10 ⁻⁵	-	-	6.0	"	8.0	
5	3.84	7.4	-	10 ⁻⁵	-	-	4.1	"	1.2	
7	0.28	3.0	-	10 ⁻⁵	-	-	4.5	"	0.5	
26	4.95	20.9	-	10 ⁻⁵	-	-	5.0	"	10.0	
52	1.09	14.4	-	10 ⁻⁵	-	-	5.7	"	11.5	
Al-saturated	59	-	10 ⁻⁷ - 10 ^{-6.1}	AlCl ₃	0.002 - 0.2	4.3	K _{Cd} Al	0.013±0.003		
205	10 ⁻⁷ - 10 ^{-6.1}	AlCl ₃	0.002 - 0.02	6.7	K _{Cd} Al	0.012±0.007				
184	10 ⁻⁷ - 10 ^{-6.1}	AlCl ₃	0.002 - 0.02	6.8	K _{Cd} Al	0.016±0.006				

Garcia-Miragaya
1980

McBride et al. 1981

Lagerwerff and
Brower 1972

Table 9-1 (Contd). ADSORPTION CONSTANTS FOR CADMIUM

Adsorbent			Adsorbate		Electrolyte		Adsorption Measurements			Reference
Identified (a)	CEC meq/100g	S ₂ A ₂ m ² /g	Conc., M	Identify	Conc., M	pH	Constants (b)	Value (c)		
Ca-saturated	59	-	10 ⁻⁷ - 10 ^{-6.1}	CaCl ₂	0.002 - 0.02	Soil 4.3	K _{Cd} K _{Ca}	3.4±0.4	Milberg et al. 1978	
	205	-	10 ⁻⁷ - 10 ^{-6.1}	CaCl ₂	0.002 - 0.02	6.7	K _{Cd} K _{Ca}	17±3		
	184	-	10 ⁻⁷ - 10 ^{-6.1}	CaCl ₂	0.02 - 0.002	6.8	K _{Cd} K _{Ca}	24±6		
Sediment										
Coastal, marine	-	-	10 ⁻⁶	Seawater	~0.7	8.1	A ₁ , k ₁ A ₂ , k ₂ A ₃ , k ₃ A ₄ , k ₄ ΣA	1) 0.025, 157 2) 0.017, 1.33 3) 0.014, 0.046 4) 0.009, 0.005 0.065	Hardy et al. 1981	
River	-	-	10 ^{-7.7} - 10 ^{-5.8}	River water	-	7.3- 8.0	A _m , K _L K _d	(2.0, 5.2) 6.1±0.8	Gardiner 1974	
			10 ^{-7.3}	"		"	"	25.0		
			10 ^{-7.7}	"		"	"	13.0		
			10 ^{-7.3}	"		"	"	8.0		
			10 ^{-6.9}	"		"	"	2.6		
			10 ^{-6.3}	"		"	"	1.2		
River, Size, mm	% O.M.									
0.44	0.6	-	10 ^{-6.7} - 10 ^{-3.8}	-	-	~7.5	A _m , K _L	17, 5.4	Ramamoorthy and Rust 1978	
0.007	3.2	-	10 ^{-6.7} - 10 ^{-3.8}	-	-	"	A _m , K _L	173, 5.4		
0.125	5.2	-	10 ^{-6.7} - 10 ^{-3.8}	-	-	"	A _m , K _L	29, 4.5		
0.16	35.7	-	10 ^{-6.7} - 10 ^{-3.8}	-	-	"	A _m , K _L	31, 5.4		
0.27	2.4	-	10 ^{-6.7} - 10 ^{-3.8}	-	-	"	A _m , K _L	10, 5.2		
0.011	1.3	-	10 ^{-6.7} - 10 ^{-3.8}	-	-	"	A _m , K _L	83, 6.0		
0.18	9.9	-	10 ^{-6.7} - 10 ^{-3.8}	-	-	"	A _m , K _L	37, 4.4		
% Clay	% O.M.									
12.6	3.34	-	10 ^{-4.1} - 10 ^{-3.1}	-	-	7.0	A _m , K _L	(36, 4.3)	Duddridge and Wathwright 1981	
13.2	3.7	-	10 ^{-4.1} - 10 ^{-3.1}	-	-	7.4	A _m , K _L	(30, 4.4)		
3.6	0.81	-	10 ^{-4.1} - 10 ^{-3.1}	-	-	6.8	A _m , K _L	(27, 4.2)		
4.9	1.06	-	10 ^{-4.1} - 10 ^{-3.1}	-	-	7.1	A _m , K _L	(26, 4.0)		

(a) H.A. = humic acid; O.M. = organic acid; O.C. = organic carbon

(b) K_F, 1/N = Freundlich constants for A = C^{1/N}, A = μmol g⁻¹; C = μM; a, b = intercept, slope of linear Isotherm; A_m = Langmuir adsorption maximum, μmol g⁻¹; K_L = Langmuir constant, log M⁻¹, A = adsorption, μmol g⁻¹; K_d = distribution coefficient, ml g⁻¹; K_a = selectivity coefficient; K₁, K₂ = surface complexation constants, log; K₁^{int} = intrinsic adsorption constants, log, K_c = affinity coefficient; K_{RC} = retention capacity; A₁, K₁ = adsorption capacity μmol g⁻¹ and rate, hr⁻¹ at different adsorption sites

(c) () = estimated values

Section 10

CHROMIUM

Chromium exists as Cr(III) and its hydrolysis products under reducing and moderately oxidizing conditions whereas under strongly oxidizing conditions it exists as Cr(VI). Attenuation mechanisms of Cr have not been extensively studied. However, Cr(III) and Cr(VI) exhibit marked differences in their geochemical behavior.

In addition to precipitation [as $\text{Cr}(\text{OH})_3$ and possibly as divalent metal chromites], Cr(III) is strongly adsorbed by soil minerals through specific adsorption and ion exchange. In contrast, Cr(VI) exists as an anion (CrO_4^{2-}) and is specifically adsorbed by iron oxides under acidic pH conditions ($\text{pH} < 7$). Thus, chromate exhibits significant subsurface mobility under neutral and basic pH regions, and is adsorbed moderately by acidic subsoils that are high in iron hydrous oxides. The catalytic reduction of Cr(VI) by soluble organic ligands and particulate organic material, and oxidation of Cr^{3+} by soil Mn oxides are important mechanisms influencing the environmental chemistry of Cr.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIES

Chromium is a multivalent element; in the environmental range in Eh and pH, only +3 and +6 valence states of Cr are important. The Cr(III) stability field extends over a wide range in pH and Eh, whereas Cr(VI) occurs only under strongly oxidizing conditions. Therefore, under moderately oxidizing to reducing conditions, Cr(III) minerals are expected to be more stable than Cr(VI) minerals. The solubility of Cr(III) minerals at moderately oxidizing conditions ($\text{pe} + \text{pH} = 10$) is given in Figure 10-1. Among the oxides and hydroxides, Cr_2O_3 is the least soluble. Chromites ($\text{XCr}_2\text{O}_4 \cdot n\text{H}_2\text{O}$, where X = divalent cation) are known to readily form under laboratory conditions. However, MgCr_2O_4 at $\text{pH} < 10$ is more soluble than Cr_2O_3 . Among all the Cr(III) solid phases for which data are available, FeCr_2O_4 is the least soluble compound at $\text{pe} + \text{pH} \leq 14$. Because FeCr_2O_4 is a common Cr(III) mineral, it is likely to be the solubility-controlling solid phase under slightly reduced conditions (Table A-5).

Figure 10-2 represents the solubility of Cr under oxidized conditions ($\text{pe} + \text{pH} = 18$). The chromates ($\text{XCrO}_4 \cdot n\text{H}_2\text{O}$), especially BaCrO_4 , PbCrO_4 , and Ag_2CrO_4 , readily

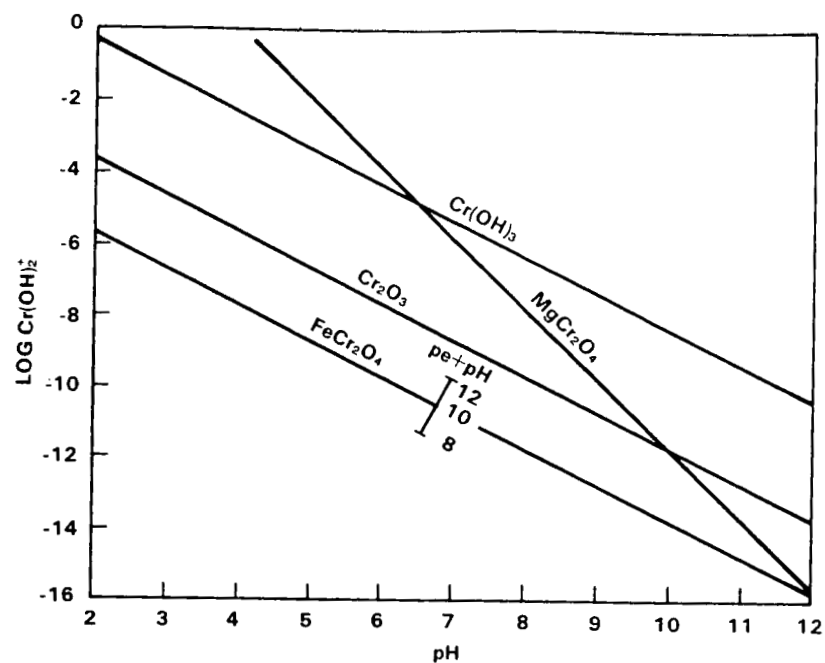


Figure 10-1. The solubility of various Cr minerals at a fixed redox potential ($\text{pe} + \text{pH} = 10$) when Fe^{2+} activity is controlled by $\text{Fe(OH)}_3(\text{am})$, and Mg^{2+} activity is fixed at $10^{-3.0}$.

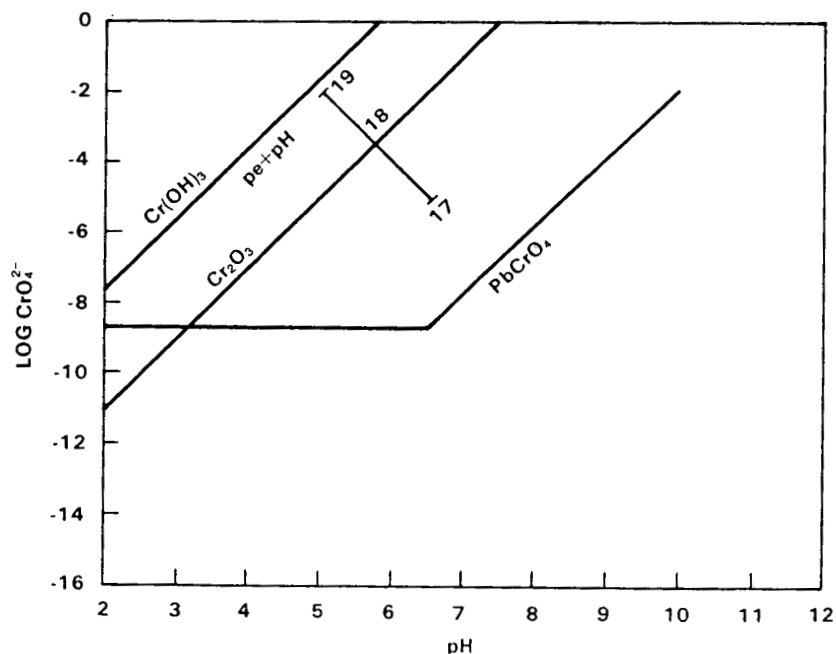


Figure 10-2. Solubility of Cr minerals at $\text{pe} + \text{pH} = 18$ as a function of pH. Pb^{2+} activities were assumed to be 10^{-5} or controlled by PbCO_3 (whichever was lower).

precipitate from solutions. Under environmental conditions, Ba^{2+} and Ag^+ aqueous activities are so low that their corresponding chromates will be too soluble to be a solubility-controlling solid. However, lead chromate may be of importance and would maintain low concentrations of CrO_4^{2-} at $\text{pH} < 8$ when the aqueous Pb^{2+} activities are assumed to be controlled by $\text{PbSO}_4(\text{c})$ [at $\text{pH} < 6$ and $\text{SO}_4^{2-} = 10^{-3} \text{ M}$] and $\text{PbCO}_3(\text{c})$ [at $\text{pH} > 6$ and CO_2 0.0003 atm]. The solubility of Cr_2O_3 decreases with the decrease in $\text{pe} + \text{pH}$. The Cr_2O_3 is a possible solubility control and would also maintain very low concentrations of CrO_4^{2-} , especially at $\text{pe} + \text{pH}$ values < 16 .

Figures 10-3 and 10-4 represent the aqueous speciation of Cr in equilibrium with $\text{Cr}_2\text{O}_3(\text{c})$ at various redox potentials. At $\text{pe} + \text{pH} = 10$ (Figure 10-3), $\text{Cr}_3(\text{OH})_4^{5+}$ appears to be the dominant ion below $\text{pH} 4.3$. However, thermodynamic data regarding the polynuclear species are judged to be unreliable because they predict unrealistic solubilities at low pH (activities of $\text{Cr}_2(\text{OH})_2^{4+}$ and $\text{Cr}_3(\text{OH})_4^{5+}$ at $\text{pH} 2$ are $10^{3.96}$ and $10^{7.37}$, respectively). Disregarding the polynuclear species, CrF_2^{2+} and Cr^{3+} are dominant below $\text{pH} 4.2$, with the Cr(III) hydrolysis species being predominant at higher pH values. Chromium(III) complexes of SO_4^{2-} , H_2PO_4^- , Cl^- , NO_3^- , and Br^- are not expected to contribute significantly to the total aqueous Cr concentrations in natural environments. The Cr(VI) species are not important at $\text{pe} + \text{pH} = 10$, but will become important in alkaline solutions when the redox potential is increased to $\text{pe} + \text{pH} = 12$. As the redox potential is further increased to $\text{pe} + \text{pH} = 18$ (Figure 10-4), the Cr(VI) species HCrO_4^- , CrO_4^{2-} and KCrO_4^- become important at pH values > 4.5 . Because equilibrium with Cr_2O_3 is assumed, the position of lines for Cr(III) species are unchanged (only the Cr^{3+} and hydrolysis species are given in Figure 10-4). The Cr(III) species are predominant at pH values < 4.5 .

PRECIPITATION/DISSOLUTION

A literature search did not reveal any studies where Cr compounds were identified as controlling aqueous Cr concentrations. However, several investigators (Krauskopf 1956; Bartlett and Kimble 1976a, 1976b; Hem 1977; Griffin et al. 1977; Cry and Olson 1977) present evidence that suggests the formation of solubility-controlling solids of Cr(III). Krauskopf (1956) quoted by Matzat and Shiraki (1978) concluded that Cr concentration in sea water is probably controlled by $\text{Cr}(\text{OH})_3$. Hem (1977) looked at the ground-water composition (reported by Robertson 1975) from Paradise Valley, Arizona and stated that the values are close to the solubility of Cr_2O_3 . Most of

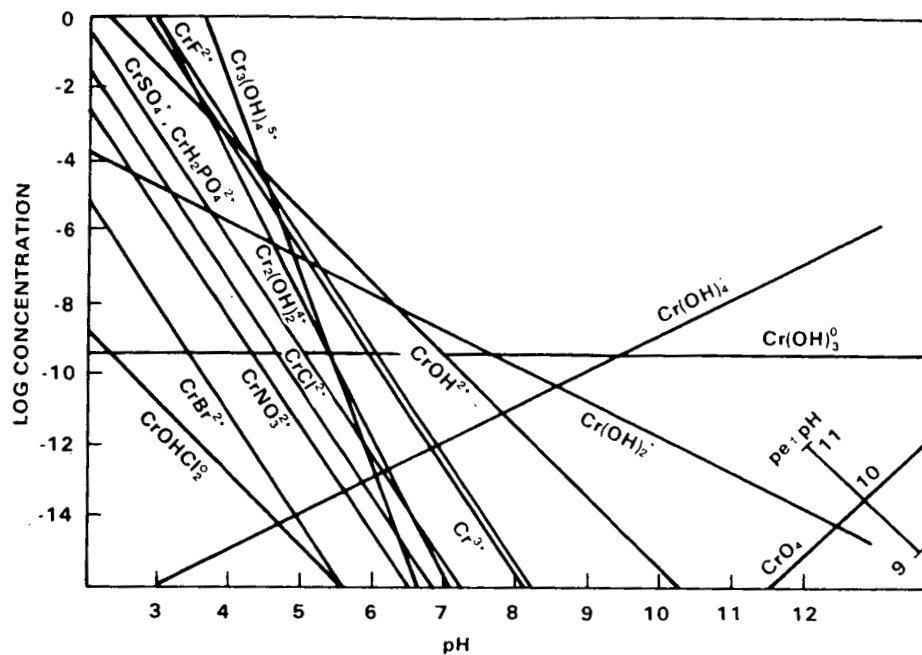


Figure 10-3. Concentrations of various Cr solution species in equilibrium with $\text{Cr}_2\text{O}_3(\text{c})$ at a fixed redox potential ($\text{pe} + \text{pH} = 10$). Assumed activities of ligands are as follows: $\text{Br}^- = 10^{-4}$, $\text{SO}_4^{2-} = \text{Cl}^- = 10^{-3}$, and $\text{H}_2\text{PO}_4^- = 10^{-5.5}$.

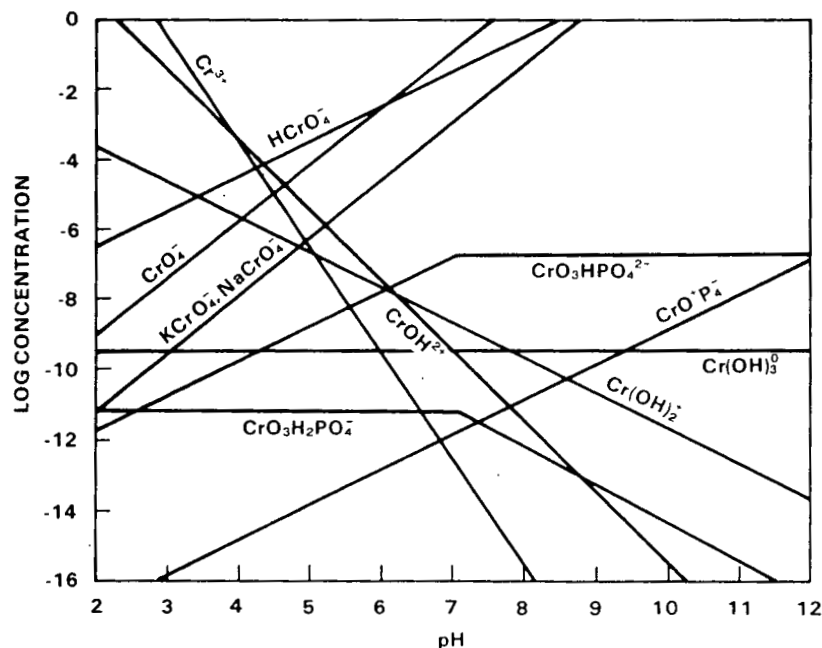


Figure 10-4. Concentrations of various Cr solution species in equilibrium with Cr_2O_3 at $\text{pe} + \text{pH} = 18$. Assumed activities of ligands were: $\text{Na}^+ = \text{K}^+ = 10^{-3}$, and total $\text{P}_4 = 10^{-5.5}$.

the Cr(III) solubility-controlling solids are either thought to be $\text{Cr}(\text{OH})_3$ or Cr(III) coprecipitated with Fe oxides. These suggestions primarily arise from:

- the thermodynamic treatment of the data where the solubility of the chromite (FeCr_2O_4) is predicted to be the lowest among the Cr minerals for which the data are available (Hem 1977)
- the simple laboratory experiments where the pH of the acidic solutions containing fairly high Cr concentrations was adjusted to higher values (Bartlett and Kimble 1976a, 1976b; Griffin et al. 1977)
- the similarity of Cr(III) ionic radius to Fe and the observations that aqueous Cr(III) is removed by $\text{Fe}(\text{OH})_3$ precipitation and that Cr during weathering is found to associate with the ferric-rich materials, such as podzolic B horizons, laterites and bauxites and iron oxides (Matzat and Shiraki 1978; Grove and Ellis 1980; Nakayama et al. 1981a, 1981b; Plotnikov and Safonov 1979).

Hem (1977) suggested that structures similar to chromite (FeCr_2O_4) with Mn replacing Fe may also exist but thermodynamic data for these solids are not available. The above studies show the importance of Fe oxides in possibly controlling Cr concentrations and also indicate the lack of accurate solubility data for different solids.

ADSORPTION/DESORPTION

The aqueous environmental chemistry of chromium is complicated by the presence of two oxidation states: Cr(III) and Cr(VI). These, in turn, exhibit contrasting adsorption behavior in soil and subsoil because of their valence. Chromium(III) exists as a cation, Cr^{3+} , and Cr(VI) as an oxyanion, CrO_4^{2-} , and, at high concentration ($>10^{-2}$ M Cr), as $\text{Cr}_2\text{O}_7^{2-}$. The chromous (Cr^{+3}) ion and its hydrolysis products and chromate (CrO_4^{2-} , HCrO_4^-) are the prominent species of concern in utility waste leachate and substrata. The theoretical equilibrium log ratio of Cr(VI)/Cr(III) is 20.5 under pH and pe conditions found for most oxygenated waters (MacNaughton 1977); this ratio is not expected to differ appreciably in surface soils. Nonequilibrium conditions may exist between these species. In addition, chromium speciation measurements in marine waters indicate significant concentrations of Cr(III) (Emerson et al. 1979). Other factors, notably reducing substrates in soil, subsoil, and geologic substrate, may be more important in controlling Cr speciation than the oxidation-reduction potential in solution.

Cr(III)

The adsorption of Cr(III) in soils has not received widespread research attention. Because of its rapid hydrolysis, precipitation as the hydroxide $\text{Cr}(\text{OH})_3$, and coprecipitation with $\text{Fe}(\text{OH})_3$, the attenuation of Cr(III) soil is normally ascribed

to solid phase formation (Hem 1977, Artiola and Fuller 1979). Adsorption, however, is an important mechanism at lower pH (<4.5) and Cr concentration (<10⁻⁶ M) (Table 10-1). Limited studies infer that Cr(III), like other cationic heavy metals, is strongly and specifically adsorbed by soil Fe and Mn oxides (Korte et al. 1976), but at higher concentrations may undergo exchange reactions with layer lattice silicates (Griffin et al. 1977). By analogy to other hydrolyzable metals and based on limited evidence (Nakayama et al. 1981a), organic material may also be an important adsorbent in soil. Chromium(III) adsorption may be influenced by Mn oxides which may catalyze oxidation to Cr(VI) (Bartlett and Kimble 1979, Nakayama et al. 1981b).

Chromium(III) adsorption increases with increasing pH (Table 10-1). On silica, this increase reflects a decreasing positive charge density of surface silanol groups and more favorable coulombic interaction between hydrolyzed Cr(III) and the oxide surface (James and Healy 1972a). The predominant adsorbing species of Cr(III) on silica are estimated to be: pH < 1.9, Cr³⁺; pH 1.9-5.0, CrOH²⁺; and pH > 5.0, Cr(OH)₂⁺ (James and Healy 1972b). Cation exchange of hydrolysis species with a lower charge density to metal ratio [e.g., Cr(OH)²⁺, Cr(OH)₂⁺, Cr₂(OH)₄²⁺, or Cr₆(OH)₁₂⁶⁺] allows more Cr(III) to bind, electrostatically, to fixed charge sites on layer lattice silicates with increasing pH (Griffin et al. 1977).

Organic ligands may form stable aqueous complexes with Cr(III) and reduce adsorption (Nakayama et al. 1981a). Certain organic acids appear particularly effective. For instance, ascorbic and citric acids reduce Cr(III) adsorption to amorphous Fe oxyhydroxide in seawater (≈pH 8) by 80 to 90% (Nakayama et al. 1981a). Several inorganic ions, however, may reduce organic complexation of Cr(III) under acid (Cl⁻) and basic (Mg²⁺, Ca²⁺) conditions when present in high concentration (>10⁻³ M) (Nakayama et al. 1981a). In soil, subsoil, and ground water, soluble humic and fulvic acids may modify Cr(III) adsorption by complexation.

Cr(VI)

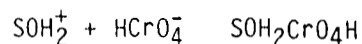
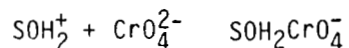
The adsorptive behavior of Cr(VI) in soil is not well documented. Several column attenuation studies (Table 10-1) qualitatively indicate that chromate (CrO₄²⁻) is relatively mobile through soil and that soil materials high in secondary hydrous oxides of Fe and Mn are more effective adsorbents (Korte et al. 1976, Artiola and Fuller 1979). Most information on Cr(VI) adsorption comes from studies with pure mineral phases; these suggest that soil minerals with high isoelectric points [e.g., αAl₂O₃, Fe₂O₃·H₂O(am)], iron oxides in general, and clay minerals to a lesser

extent, adsorb Cr(VI) at low-to-medium pH levels (pH 2 to 7) (Leckie et al. 1980, Davis and Leckie 1980, MacNaughton 1977, Mayer and Schick 1981, Griffin et al. 1977).

Chromate adsorption on model absorbents is strongly pH dependent and is affected by ionic strength and the surface protonation characteristics of the adsorbent. Chromium(VI) adsorbs weakly on SiO_2 ($\text{pH}_{\text{IEP}} = 2.0$), which has a negative surface charge at all but the lowest pH values, and strongly on $\alpha\text{Al}_2\text{O}_3$ ($\text{pH}_{\text{IEP}} = 9.0$) and $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{am})$ ($\text{pH}_{\text{IEP}} = 7.5$) which carry positive charge over a greater pH range (MacNaughton 1977, Davis and Leckie 1980). Adsorption on TiO_2 ($\text{pH}_{\text{IEP}} = 7.0$) is significantly less than Al and Fe oxides (MacNaughton 1977). On $\alpha\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{am})$ fractional adsorption may rapidly decrease from near 100% at low-to-intermediate pH values (5 to 7) to near 0 at pH 8 (MacNaughton 1977; Davis and Leckie 1980). Increasing electrolyte concentrations (10^{-3} to 10^{-1} M) reduces Cr(VI) adsorption by amphoteric model adsorbents (oxides) through reduction in surface electric potential (Mayer and Schick 1981, MacNaughton 1977; Davis and Leckie 1980). In contrast, increasing electrolyte concentration and compression of the electric double layer may lead to increased Cr(VI) adsorption in layer lattice silicates with predominantly negative charge (Griffin et al. 1977).

The presence of competing and, less commonly, complexing ions may significantly alter CrO_4^{2-} adsorption. Although SO_4^{2-} is absorbed less strongly on $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{am})$ than CrO_4^{2-} , SO_4^{2-} may compete for adsorption sites when present in higher concentration (Leckie et al. 1980). Phosphate exhibits a more substantial effect on CrO_4^{2-} adsorption by $\alpha\text{-Al}_2\text{O}_3$ (MacNaughton 1977), reducing sorption by around 50% when present in equal concentration. Information on effects of complexing ions on Cr(IV) sorption is almost nonexistent, though adsorption of ion pairs (e.g., CaCrO_4^0 , KHCrO_4^0) is suggested as one possible mechanism for high removal of Cr(VI) from fly ash leachate by $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{am})$ (Leckie et al. 1980).

Surface complexation or site-binding models (Davis 1978; Davis and Leckie 1980; Benjamin and Bloom 1981) suggest two plausible surface reactions which may occur during adsorption of Cr(VI) on Al and Fe oxide surfaces (Table 10-1):



In spite of its lower isoelectric point, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{am})$ adsorbs CrO_4^{2-} more strongly than Al_2O_3 (MacNaughton 1977, Davis 1978). Chromium(VI) adsorption on layer lattice silicates follows the Langmuir isotherm; when calculated on a surface area basis, montmorillonite and kaolinite adsorb comparable amounts of Cr(VI) from landfill leachate (Griffin et al. 1977). The adsorption capacity of clay minerals varies with pH but ranges between 0.29 to 3.67 $\mu\text{mole/g}$ for kaolinite and 0.98 to 12.8 $\mu\text{mole/g}$ for montmorillonite (Table 10-1). The adsorption behavior of Cr(VI) in soils is complicated by redox changes which may occur concurrent to adsorption. For instance, Cr(VI) is likely reduced to Cr(III) in sediment by reaction with organic material or, in some cases, H_2S , and Cr(III) is then rapidly and strongly adsorbed (Mayer and Schick 1981). A similar reaction may occur in soil at low pH and high organic content (Bartlett and Kimble 1976b).

Table 10-1. ADSORPTION CONSTANTS FOR CHROMIUM

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurement		References
Identity	CEC meq/100 g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (a)	Values	
Fe ₂ O ₃ ·H ₂ O (am)	-	182	10 ^{-6.3} Cr(VI)	NaNO ₃	0.1	4-9	K ^{Int} _{CrO₄} , K ^{Int} _{HCrO₄}	5.5, 6.5	Davis and Leckie 1980
Fe ₂ O ₃ ·H ₂ O (am)	-	~182	10 ⁻⁵ Cr(VI)	NaNO ₃	0.1	4-9	K ^{Int} _{CrO₄} , K ^{Int} _{HCrO₄}	6.8, 6.4	Benjamin and Bloom 1981
			10 ⁻⁴ Cr(VI)	NaNO ₃	0.1		K ^{Int} _{CrO₄} , K ^{Int} _{HCrO₄}	9.3, 5.2	
α Al ₂ O ₃	-	204	10 ^{-3.7} Cr(VI)	NaNO ₃	10 ⁻³ -10 ⁻⁴	3-10	K ^{Int} _{CrO₄} , K ^{Int} _{HCrO₄}	3.1, 3.1	Davis 1978
Kaolinite	15.1	34.2	10 ^{-4.0} - 10 ^{-2.2} Cr(VI)	leachate		3	A _m	3.64	Griffin et al. 1977
						4		2.50	
						5		2.22	
						7		0.98	
						3		1.79	
						4		0.85	
						5		0.62	
						7		0.29	
			10 ^{-3.3} - 10 ^{-1.8} Cr(III)	leachate		3.0	A _m	96.3	
						4.0		283	
						2.5		63.5	
						3.0		96.3	
			Cr(NO ₃) ₃			4.0		206	

Table 10-1 (Contd). ADSORPTION CONSTANTS FOR CHROMIUM

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurement		References
Identity	CEC meq/100 g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (a)	Values	
Montmorillonite	79.5	86.2	10 ^{-4.0} - 10 ^{-2.2} Cr(VI)	leachate		3	A _m	12.8	
						4		10.3	
						5		8.03	
						7		3.26	
					K ₂ CrO ₄	3		3.64	
			10 ^{-3.3} - 10 ^{-1.3} Cr(III)	leachate		4	A _m	2.50	
						5		2.22	
						7		0.98	
					Cr(NO ₃) ₃	3.0		632	
						4.0		2622	
Silica	-	75	10 ⁻⁴	-	-	3-6	*K _{Ca} ^{Int}	-4.1, (3.1)	James and Healy 1972b.
							K _{Ca} ^{Int}		
							*K _{OH} ^{Int}	-5.9, (5.2)	
							K _{OH} ^{Int}		
							*K _{(OH)₂} ^{Int}		
							K _{(OH)₂} ^{Int}		

(a) K^{Int} = Intrinsic adsorption constant of ionic species, logA_m = Langmuir adsorption maximum, μmol g⁻¹

(b) () - estimated values.

Section 11

COPPER

Copper (Cu) in aqueous solutions can exist in a +1 or +2 valence state. Under oxidizing conditions (pH values ≤ 7), Cu^{2+} is the dominant species with hydrolysis species of Cu^{2+} becoming dominant at higher pH values. Precipitation/dissolution mechanisms have not been adequately studied. However, many studies suggest that the solution concentrations are prominent among the compounds available for adsorption/desorption. At low environmental concentrations, adsorption/desorption is controlled by a number of soil constituents, such as organic matter, iron and Mn-oxides, through complexation and specific adsorption. Copper ferrites have very low solubilities but information on their solubility is not available. The effects of ion competition, aqueous solution, and ligand adsorption are not well understood. Preliminary studies of copper in fly ash leachates on iron oxyhydroxides indicate increased adsorption at high pH (> 6) and decreased adsorption at low pH (< 6) as compared with other systems.

STABILITY OF SOLID AND AQUEOUS SPECIES

Copper exists in two oxidation states: Cu(I) predominates in oxidizing conditions. As a result, Cu(II) dominates in reducing conditions. The relative stability of the solid phases of Cu(I) and Cu(II) depends upon the conditions. Lindsay (1979) calculated the relative stability of Cu(I) and Cu(II) species in ground waters. His results show that under oxidizing conditions cuprous species are very stable, while under reducing conditions cuprous species are the stable phase.

Relative abundance of different Cu species in equilibrium with aqueous Cu species (Figures 11-1 and 11-2) using the geochemical model MINTEQA2 (Allison et al., 1991) were plotted in the figure. The results show that at pH values > 4 , Cu(I) is the stable phase, while at pH values < 4 , Cu(II) is the stable phase.

Table 10-1 (Contd). ADSORPTION CONSTANTS FOR CHROMIUM

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurement		References			
Identity	CEC meq/100 g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants ^(a)	Values				
Montmorillonite	79.5	86.2	10 ^{-4.0} - 10 ^{-2.2} Cr(VI)	leachate		3	A _m	12.8				
						4		10.3				
						5		8.03				
						7		3.26				
						K ₂ CrO ₄		3		3.64		
			4	2.50								
			5	2.22								
			7	0.98								
			10 ^{-3.3} - 10 ^{-1.3} Cr(III)	leachate		3.0	A _m	632				
						4.0		2622				
						Cr(NO ₃) ₃				2.5	345	
										3.0	649	
						4.0	2689					
Silica	-	75	10 ⁻⁴			-	-	3-6	*K ^{Int} _{Ca}	-4.1, (3.1)	James and Healy 1972b	
									K ^{Int} _{Ca}			
				*K ^{Int} _{OH}	-5.9, (5.2)							
				K ^{Int} _{OH}								
				*K ^{Int} _{(OH)₂}								
				K ^{Int} _{(OH)₂}								

(a) K^{Int} = Intrinsic adsorption constant of ionic species, log A_m = Langmuir adsorption maximum, $\mu\text{mol g}^{-1}$

(b) () - estimated values.

Section 11

COPPER

Copper (Cu) in aqueous solutions can exist in a +1 or +2 valence state. Under oxidizing conditions (pH values ≤ 7), Cu^{2+} is the dominant species with hydrolysis species of Cu^{2+} becoming dominant at higher pH values. Precipitation/dissolution attenuation mechanisms have not been adequately studied. However, many studies dealing with adsorption/desorption suggest that the solution concentrations are solubility controlled. In these studies, $\text{Cu}(\text{OH})_2$ is prominent among the compounds implicated. Copper ferrites have very low solubilities but information on their formation in geologic environments is not available. At low environmental concentrations, Cu is strongly adsorbed by a number of soil constituents, such as organic matter and Fe- and Mn-oxides, through complexation and specific adsorption. Copper adsorption strongly depends on pH because CuOH^+ rather than Cu^{2+} is the preferred surface species for many adsorbents. The effects of ion competition, aqueous complexation, and ligand adsorption are not well understood. Preliminary studies of Cu adsorption from fly ash leachates on iron oxyhydroxides indicate increased adsorption at low pH (< 6) and decreased adsorption at high pH as compared with simple electrolyte systems.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIES

In solution, copper exists in two oxidation states: Cu(I) predominates in relatively reducing conditions while Cu(II) dominates in oxidizing conditions. As a result, the solubility of the solid phases of Cu(I) and Cu(II) depends upon the redox potential. Recently Lindsay (1979) calculated the relative stability of different Cu solids. His results show that under oxidizing conditions, soil-Cu and cupric ferrite (CuFe_2O_4) are very stable, while under reducing conditions cuprous ferrite ($\text{Cu}_2\text{Fe}_2\text{O}_4$) is the stable phase.

To determine the relative abundance of Cu(I) and Cu(II) species in ground waters representative of leachates, activities of different Cu species in equilibrium with CuFe_2O_4 at two different Eh values were plotted (Figures 11-1 and 11-2) using the thermodynamic data (Ball et al. 1980) contained in the geochemical model MINTEQA (Felmy et al. 1983). Under reducing conditions ($p_e + \text{pH} = 7$) and at pH values > 4 ,

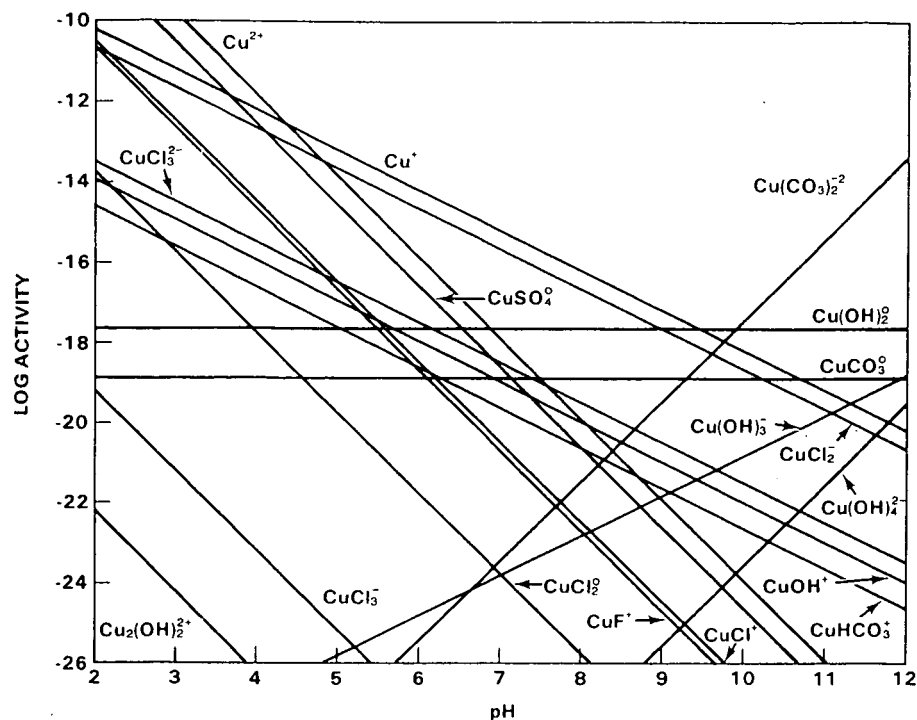


Figure 11-1. Activities of different Cu species in equilibrium with cupric ferrite (CuFe_2O_4) under reducing conditions ($p_e + \text{pH } 7$) when activities of $\text{SO}_4^{2-} = \text{Cl}^- = 10^{-3}$, $\text{F}^- = 10^{-4}$, $\text{CO}_2(\text{gas}) = 10^{-3.52}$ atmospheres.

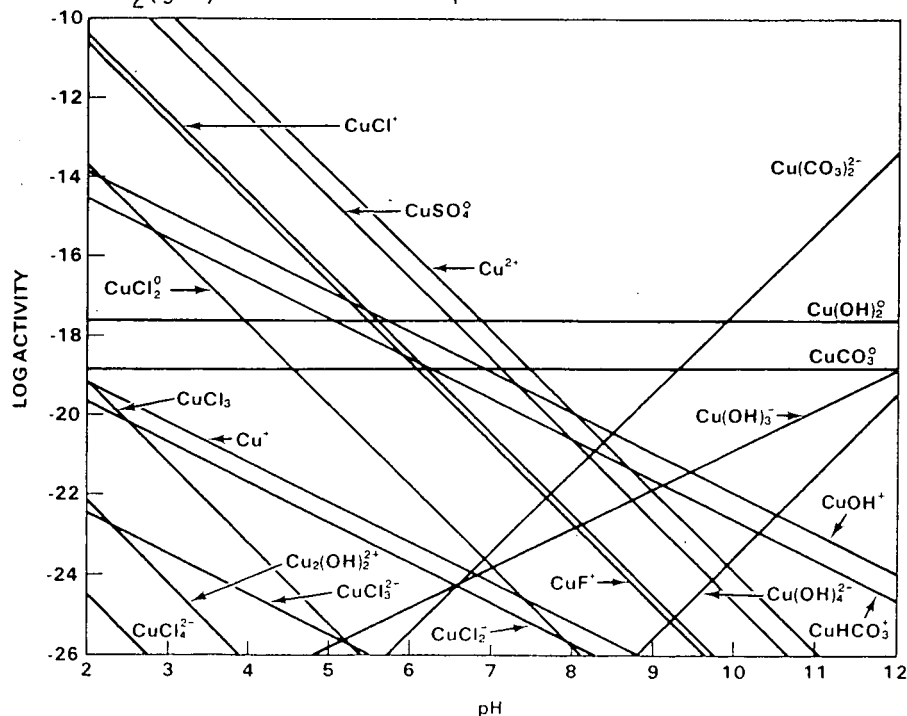


Figure 11-2. Activities of different Cu species in equilibrium with cupric ferrite (CuFe_2O_4) under oxidizing conditions ($p_e + \text{pH } 16$) when activities of $\text{SO}_4^{2-} = \text{Cl}^- = 10^{-3}$, $\text{F}^- = 10^{-4}$, $\text{CO}_2(\text{gas}) = 10^{-3.52}$ atmospheres.

Cu^{2+} and Cu(II) complexes with SO_4^{2-} , Cl^- , OH^- , HCO_3^- , CO_3^{2-} , and F^- do not contribute significantly to total soluble Cu (Figure 11-1). Under reducing conditions, Cu^+ and Cu(I) complexes are dominant at pH values between 4.3 and 9.5. Cu(I) forms a very strong complex with Cl^- . As a result, CuCl_2^- is one of the dominant species in solutions of pH values between 4.3 and 9. Data for Cu-polysulfide complexes [such as $\text{Cu}(\text{S}_4)_2^{3-}$ and $\text{CuS}_4\text{S}_5^{3-}$] are included in the model data base (Ball et al. 1980). (These complexes may be important under reducing conditions but are not plotted in Figure 11-1.) Under oxidizing conditions (pe + pH 16) Cu^{2+} is the dominant species below pH values of about 7; at pH values between 7 and 10, $\text{Cu}(\text{OH})_2^0$ appears to be the dominant species (Figure 11-2). Baes and Mesmer (1976) report, however, that reliable estimates of the formation constant of Cu(II)-hydroxo complexes are not available. All of the other Cu(II) complexes (such as with SO_4^{2-} , F^- , HCO_3^-) do not contribute significantly to the total soluble Cu.

PRECIPITATION/DISSOLUTION

The retention of Cu by montmorillinite (Bingham et al. 1964) and some soils (Abd-Elfattah and Wada 1981) have been observed to be consistent with the formation of a Cu solid phase such as $\text{Cu}(\text{OH})_2$. Farrah and Pickering (1976) suspected the formation of Cu oxides and phosphate solid phases during adsorption of Cu on kaolinite. The behavior of the Cu in the kaolinite suspensions was consistent with solid phase formation, and the solubility products calculated by Farrah and Pickering (1976) were similar to published values. Frost and Griffin (1977) examined the removal of Cu from leachates by clay minerals and concluded that precipitation is an important removal mechanism at pH values greater than 6.5. Carvallaro and McBride (1978) stated that solution levels of Cu^{2+} maintained by adsorption onto soils were below saturation levels of Cu(II) minerals (specifically $\text{Cu}(\text{OH})_2$ and $\text{Cu}_2(\text{OH})_2\text{CO}_3$). However, the observed Cu^{2+} levels are very near saturation for CuFe_2O_4 and represent supersaturation with respect to soil-Cu (Lindsay 1979). The formation of a Cu oxide was implicated by Hatton and Pickering (1980) after observing a minimum Cu solubility at pH 4.5 in clay-humic acid mixtures. Dhillon et al. (1981) found that their experiments involving the adsorption of Cu by alkaline soils was complicated by the formation of Cu solids [$\text{Cu}(\text{OH})_2$ or $\text{Cu}_2(\text{OH})_2\text{CO}_3$]. Although a discrete Cu solid phase was not observed, it is impossible to distinguish between precipitation and adsorption because both precipitation and adsorption obey the Langmuir equation under the conditions of Dhillon et al.'s (1981) experiments. McBride (1982) measured the adsorption of Cu^{2+} on aluminum hydroxide and oxyhydroxides as a function of pH. Only adsorption reactions of Cu^{2+} were observed for noncrystalline alumina and bohemite, but precipitation of $\text{Cu}(\text{OH})_2$ was observed in the case of gibbsite.

Leckie et al. (1980) studied the adsorption of Cu by α -SiO₂ and observed that at high Cu concentrations (5×10^{-5} M), precipitation of Cu(OH)₂ rather than adsorption appears to control Cu concentrations.

ADSORPTION/DESORPTION

Copper is strongly adsorbed in soil by three prominent retention mechanisms: complexation by soil organic matter, specific adsorption, and ion exchange. A number of investigators suggest that in surface soils, soil organic matter is the dominant factor controlling Cu adsorption (McLaren and Crawford 1973, Petruzelli et al. 1978, Ramamoorthy and Rust 1978). In fact, Hg and Cu appear to have greater affinity for the soil organic fraction than all other cationic heavy metals (Kerndorff and Schnitzer 1980). At low aqueous concentrations of Cu and in soils or subsoils low in organic material, specific adsorption to soil Fe, Al, and Mn oxides may be the prominent retention mechanism (McLaren and Crawford 1973; Oakley et al. 1981; Davis and Leckie 1978; McKenzie 1980; McBride 1982). Manganese oxides have a high specific adsorption capacity for Cu (Oakley et al. 1981; McKenzie 1980). Layer lattice silicates retain Cu primarily by ion exchange (McLaren et al. 1981; Frost and Griffin 1977; El-Sayed et al. 1979; Oakley et al. 1981). As a result, ion exchange is an important adsorption mechanism at higher Cu solutions where the specific adsorption and complexation capacity of soil hydrous oxides and organic matter has been exceeded. Soil pH has an important effect on Cu adsorption (e.g., Sadiq 1981), in that it controls Cu solution speciation and hydrolysis, and surface charge distribution on amphoteric soil hydrous oxides.

The pH dependency of Cu adsorption varies on different model adsorbents (Table 11-1). The adsorption of Cu by organic matter (McLaren et al. 1981) or by oxides with low isoelectric points (pH_{IEP}), such as silica (Schindler et al. 1976; Bourg and Schindler 1978; Bourg et al. 1979; Bourg and Schindler 1979; Huang et al. 1977) or Mn oxides (McKenzie 1980; McLaren and Crawford 1973) shows little dependency on pH. In contrast, the adsorption of Cu on Fe oxides displays a marked adsorption "edge" where adsorption increases from near 0% to 100% in two pH units. The adsorption edge depends on the experimental conditions (e.g., concentration of Cu or the oxide), but occurs between pH 3 and 6 (McLaren et al. 1981; McLaren and Crawford 1973; Balistrieri and Murray 1982; Forbes et al. 1976; McKenzie 1980; Kinniburgh et al. 1976; Swallow et al. 1980; Benjamin and Leckie 1982a). Similar adsorption edges are observed on aluminum oxides (McBride 1982; Huang et al. 1977; Kinniburgh et al. 1976; Elliott and Huang 1980) and clay minerals (Oakley et al. 1981; McLaren et al. 1981; McLaren and Crawford 1973; Frost and Griffin 1977; Kishk and Hassan 1973; Farrah and Pickering 1976; Farrah and Pickering 1977; O'Connor and

Kester 1975). The pH dependent adsorption of Cu is ascribed to the adsorption of hydroxo complexes (e.g., CuOH^+) which are more strongly bound to the surface than the free hydrated ion (Cu^{+2}) (McKenzie 1980, Davis and Leckie 1978).

The presence of relatively high concentrations (10^{-3} - 10^{-2}M) of other divalent cations, such as Ca, reduces the adsorption of Cu (10^{-5} - 10^{-4}) by soil (Cavallaro and McBride 1978), Fe oxides (goethite) (McLaren and Crawford 1973), and clay minerals (Frost and Griffin 1977). The clay mineral bentonite appears to have nearly equal preference for Cu and Ca on exchange sites; the exchange of Cu is reduced in the presence of other divalent cations (El-Sayed et al. 1970). The specific adsorption of Cu on goethite (Balistrieri and Murray 1982b) and amorphous iron oxyhydroxide (Benjamin and Leckie 1982) is unaffected by the presence of equal concentrations of Pb, Zn, and Cd suggesting that the metals are each bound by a specific surface site. With electrolytes composed of monovalent ions (e.g., NaClO_4), increasing the ionic strength of the aqueous phase has minimal effect on Cu adsorption by silica, Fe oxides and clay minerals.* In contrast increasing ionic strength reduces Cu adsorption on Al oxides (McBride 1982, Huang et al. 1977, Kinniburgh et al. 1976, Elliot and Huang 1979).

Inorganic and organic ligands have a variable effect on Cu adsorption by soils and model adsorbents (Table 11-1). In most cases, monovalent anions (NO_3^- , Cl^- , ClO_4^-) have little influence on Cu adsorption by Fe oxides (Forbes et al. 1976, McKenzie 1980, Swallow et al. 1980, Benjamin and Leckie 1982a). However, Bowden et al. (1977) found that Cl^- (10^{-2} , 10^{-3}M) increased Cu adsorption on goethite, possibly by adsorption of CuCl^+ complexes. The anion HPO_4^{2-} has little effect on Cu retention by kaolinite where exchange processes predominate adsorption (Farrah and Pickering 1976). Sulfate increases adsorption of Cu by goethite (Balistrieri and Murray 1982) possibly by reducing net positive surface charge through specific adsorption. Though complex-forming organic ligands (e.g., EDTA) may reduce Cu adsorption by reducing the free ion activity (Bourg and Schindler 1978, Bourg and Schindler 1979, Farrah and Pickering 1976), both positive and negatively charged organic Cu complexes may be adsorbed electrostatically on positively charged oxide surfaces and negatively charged clays (Bourg et al. 1979; Elliot and Huang 1979; Elliot and Huang 1981; Farrah and Pickering 1976), some of which may increase total Cu

*Silica--Schindler et al. 1976; Bourg and Schindler 1978; Bourg et al. 1979; Bourg and Schindler 1979; Huang et al. 1977.

Fe oxides--McLaren and Crawford 1973a; Balistrieri and Murray 1982; Forbes et al. 1976; Kinniburgh et al. 1976; Swallow et al. 1980; Benjamin and Leckie 1982a

Clay minerals--McLaren and Crawford 1973; Oakley et al. 1981; McLaren et al. 1981.

retention. Humic acids reduce Cu adsorption on kaolinite by interaction with the clay mineral surface and formation of aqueous Cu-humate complexes (Gupta and Harrison 1982).

The Langmuir isotherm is often used to describe Cu adsorption by soil (McLaren and Crawford 1973; Cavallaro and McBride 1978; Petruzzelli et al. 1978; Ramamoorthy and Rust 1978). In some cases, however, adsorption is more adequately described using the Freundlich equation, suggesting that the adsorption surface is heterogeneous and multiple sites exist (Sanders 1980; Sidle and Kardos 1977; Benjamin and Leckie 1981). An extensive investigation of Cu adsorption by organic material (Sanders 1980) indicates that a two-site Langmuir equation is most appropriate. It appears likely that two distinct binding sites exist in organic material or that two aqueous species of Cu undergo adsorption. Use of an activity-corrected Langmuir isotherm would provide data with more generic applicability, alleviating some pH dependency due to changes in solution speciation.

Models which describe adsorption of Cu by mineral surfaces including goethite (Balistriero and Murray 1982), amorphous iron oxyhydroxide, aluminum oxide and silica (Davis and Leckie 1978) and clay minerals (Steger 1973) are based on the adsorption of Cu^{2+} and the simultaneous formation and adsorption of CuOH^+ . The adsorption models do not distinguish between adsorption of CuOH^+ present in solution and surface hydrolysis of adsorbed Cu^{2+} , because these are thermodynamically inseparable. A surface complexation model which describes Cu adsorption by silica through formation of mono- and bi-dentate surface complexes (Schindler et al. 1976; Bourg and Schindler 1978; Bourg et al. 1979; Bourg and Schindler 1979), can also be adequately explained by Cu^{2+} and CuOH^+ adsorption (Davis and Leckie 1978). Similarly, the pH dependent adsorption of Cu on goethite and the release of protons that accompanied adsorption was quantitatively described using a model where CuOH^+ was the only adsorbing species (Barrow et al. 1981).

Table 11-1. ADSORPTION CONSTANTS FOR COPPER

Adsorbent			Adsorbate		Electrolyte		Adsorption Measurements		Reference
Identity (a)	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
<u>Clay Minerals</u>									
Bentonite, Ca-form	-	-	0 - 0.01	-	-	4.5-5.0	K ^{Cu} _{Ca}	0.957	El-Sayad et al. 1970
-	-	-	0 - 10 ^{-5.3}	Seawater	~0.7	8	A _m , K _L , K _d	(140, 5.7), 43	Oakley et al. 1981
Montmorillonite	-	-	10 ^{-5.8} - 10 ^{-3.8}	CaCl ₂	0.05	6	A _m	(3.3)	McLaren et al. 1981
			10 ^{-5.8} - 10 ^{-3.8}	CaCl ₂	0.05	5.5	A _m , K _L	5.8, 4.8	McLaren and Crawford 1973a
Montmorillonite, Na-form	-	100	10 ^{-6.5}	Seawater	~0.7	8	K _d	50	Takemitsu 1979
Bentonite	-	-	10 ^{-5.4} - 10 ^{-3.5}	CaOA	0.025	4.3-5.9	A ^I _m , K ^I _L (Cu)	8.2, 4.8	Steger 1973
							A ^{II} _m , K ^{II} _L (Cu)	2.2, 7.0	
							K ^{III} _L (CuOH)	14.6	
Kaolinite, H-form	-	-	Trace	-	-	6.4	K _d	43	Gupta and Harrison 1982
				Humic Acid	0.5 µg/l	6.4	K _d	3.2	
					1.0 µg/l	6.4	K _d	2.5	
					71.5 µg/l	6.4	K _d	2.2	
Kaolinite	-	-	10 ^{-5.8} - 10 ^{-3.8}	CaCl ₂	0.05	6	A _m	(0.2)	McLaren et al. 1981
			10 ^{-5.8} - 10 ^{-3.8}	CaCl ₂	0.05	5.5	A _m , K _L	1.9, 4.5	McLaren and Crawford 1973a
Illite	-	-	10 ^{-5.8} - 10 ^{-3.8}	CaCl ₂	0.05	6	A _m	(1.6)	McLaren et al. 1981
			10 ^{-5.8} - 10 ^{-3.8}	CaCl ₂	0.05	5.5	A _m , K _L	8.3, 4.5	McLaren and Crawford 1973a
Halloysite	-	-	10 ^{-5.8} - 10 ^{-3.8}	CaCl ₂	0.05	5.5	A _m , K _L	12.8, 4.4	
<u>Silica</u>									
-	160	10 ^{-3.8}	-	NaClO ₄	1.0	4.5-8.4	*K ^S ₁ Si-OCu	-5.5	Schindler et al. 1976
							*β ^S ₂ (Si-O) ₂ Cu	-11.2	
							K ^{int} _{Cu} , K ^{int} _{CuOH}	(1.7, 3.7)	Stumm et al. 1976
-	160	10 ^{-3.8}	-	NaClO ₄	1.0	5-9			
				+Ethylene-Diamine	-	-	*K ^S ₁ Si-OCuEn	-5.2	Bourg and Schindler 1978
					10 ^{-3.8}	-	*β ^S ₂ (Si-O) ₂ CuEn	-12.6	

Table 11-1 (Contd). ADSORPTION CONSTANTS FOR COPPER

Adsorbent			Adsorbate		Electrolyte			Adsorption Measurements		Reference
Identity (a)	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)		
Silica (cont'd)	-	248	10 ^{-3.7}	NaNO ₃	0.1	2-7	*K ₁ ^S SI-OCu	-4.9	Bourg et al. 1979	
							*K ₂ ^S (SI-O) ₂ Cu	-10.2		
				+2,2 Bipyridyl	10 ^{-4.1} - 10 ^{-3.5}		*K ₁ ^S SI-OCuBipy	-2.2		
							*K ₁ ^S SI-OCu(Bipy) ₂	0.4		
							*K ₂ ^S (SI-O) ₂ CuBipy	-6.6		
							*K ₂ ^S (SI-O) ₂ Cu(Bipy) ₂	(-8.9)		
-	-	10 ⁻⁶	-	-	-	K _{Cu} ^{Int} , K _{CuOH} ^{Int}	2.8, 6.6	Davis and Leckie 1978		
<u>Alumina</u>										
-	-	10 ⁻⁶	-	-	-	-	K _{Cu} ^{Int} , K _{CuOH} ^{Int}	6.4, 9.7	Davis and Leckie 1978	
-	-	-	-	NaClO ₄	0.1	-	*K ₁ ^S Al-OCu	-2.1	Stumm et al. 1976	
							*K ₂ ^S (Al-O) ₂ Cu	-7.0		
							K _{Cu} ^{Int} , K _{CuOH} ^{Int}	(7.4, 10.2)		
<u>Fe Oxides</u>										
α-FeOOH	-	51.8	10 ^{-6.5} - 10 ^{-5.5}	Seawater	~0.7	8	*K _{Cu} ^{Int} , *K _{CuOH} ^{Int}	-3, -7	Ballistreri and Murray 1982	
Fe ₂ O ₃ ·H ₂ O(am)	-	-	10 ⁻⁶	-	-	-	K _{Cu} ^{Int} , K _{CuOH} ^{Int}	6.5, 9.6	Davis and Leckie 1978	
Fe oxide (fresh)	-	-	-	CaCl ₂	0.5	5.5	A _m , K _L	126, 4.9	McLaren and Crawford 1973a	
Fe-Mn concretions	-	-	-	CaCl ₂	0.05	5.5	A _m , K _L	142, 4.6		
Goethite	-	-	10 ^{-4.5}	NaNO ₃	0.08	4-6	K _C ^{Int}	-2.1	Forbes et al. 1976	
Goethite	-	-	10 ⁻⁴	KNO ₃	0.01	-	A _m , K _L	(133, 3.1)	McKenzie 1980	
Hematite	-	-	10 ⁻⁴	KNO ₃	0.01	-	A _m , K _L	(28, 2.9)		
Fe ₂ O ₃ ·H ₂ O(am)	-	-	0 - 10 ^{-4.5}	Seawater	~0.7	8	A _m , K _L	(1220, 5.3)	Oakley et al. 1981	
Fe ₂ O ₃ ·H ₂ O(am)	-	215	10 ^{-6.5}	Seawater	~0.7	8	K _d	7000	Takematsu 1979	
Fe(OH) ₃	-	-	-	Seawater	~0.7	8	K _d	205	Oakley et al. 1981	

Table 11-1 (Contd). ADSORPTION CONSTANTS FOR COPPER

Adsorbent			Adsorbate		Electrolyte		Adsorption Measurements		Reference
Identity (a)	CEC meq/100g	S ₂ A ₂ m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
<u>Mn Oxides</u>									
MnO ₂ (fresh)	-	-	0 - 10 ^{-3.8}	CaCl ₂	0.05	5.5	A _m , K _L	1080, 5.4	McLaren and Crawford 1973a
δ-MnO ₂	-	98	-	KNO ₃	0.1	5.0	A _m , K _L	(1670, 3.8)	McKenzie 1980
α-MnO ₂ (K ₂ Mn ₈ O ₁₆)	-	206	-	KNO ₃	0.1	5.0	A _m , K _L	(1720, 3.4)	
γ-MnOOH	-	56	10 ^{-6.5}	Seawater	~0.7	8	K _d	8000	Takemitsu 1979
7λMnO ₂	-	33	10 ^{-6.5}	Seawater	~0.7	8	K _d	7000	
δ-MnO ₂	-	61	10 ^{-6.5}	Seawater	~0.7	8	K _d	10,000	
Hydrous MnO ₂	-	-	0 - 10 ^{-5.5}	Seawater	~0.7	8	K _d	7300	Oakley et al. 1981
<u>Ti Oxide</u>									
Rutile	-	-	-	NaClO ₄	1.0	-	*K ₁ ^S Ti-OCu	-1.5	Stumm et al. 1976
							*B ₂ ^S (Ti-O) ₂ Cu	-5.0	
							K _{Cu} ^{Int} , K _{CuOH} ^{Int}	(6.3, 10.5)	
<u>Organic Matter</u>									
Peat	-	-	0 - 10 ^{-3.8}	CaCl ₂	0.05	5.5	A _m , K _L	184, 5.0	McLaren and Crawford 1973a
	-	-	-	-	-	-	A _m , K _L	(290, 4.9)	Bunzl et al. 1976
Humic acid (commercial)	-	-	0 - 10 ^{-5.9}	Seawater	~0.7	8	A _m , K _L K _d	(640, 6.4) 366	Oakley et al. 1981
Humic acid (soil)	-	-	10 ^{-4.3} - 10 ^{-3.3}	-	-	2.4	A _m , K _L	(29, 5.6)	Kerndorff and Schnitzer 1980
Humic material from: composted alfalfa (H ₂ O extr.)	-	-	10 ^{-5.5} - 10 ^{-3.6}	KNO ₃	0.1	6	A _m ^I , K _L ^I , A _m ^{II}	2100, 4.3, 1280	Sanders, 1980
Colloidal								4.4, 940, 0.22	
Dialysable	-	-	10 ^{-5.5} - 10 ^{-3.6}	KNO ₃	0.1	6	K _L ^{II} , K _F , 1/N	3440, 4.0, 1350, 6.2, 820, 0.27	
plus soil Colloidal (KOH extr.)	-	-	10 ^{-5.5} - 10 ^{-3.6}	KNO ₃	0.1	6	"	1670, 4.0, 610 5.8, 300, 0.35	
Dialysable (H ₂ O extr.)	-	-	10 ^{-5.5} - 10 ^{-3.6}	KNO ₃	0.1	6	"	1730, 4.0, 290 6.2, 200, 0.41	

Table 11-1 (Contd). ADSORPTION CONSTANTS FOR COPPER

Adsorbent			Adsorbate		Electrolyte			Adsorption Measurements		Reference
Identity ^(a)	CEC meq/100g	S ₂ A ₂ m ² /g	Conc., M	Identity	Conc., M	pH	Constants ^(b)	Value ^(c)		
Soil only										
Colloidal (KOH extr.)	-	-	10 ^{-5.5} - 10 ^{-3.6}	KNO ₃	0.1	6	"	2440, 4.0, 750 5.7, 330, 0.37		
Dialysable (KOH extr.)	-	-	10 ^{-5.5} - 10 ^{-3.6}	KNO ₃	0.1	6	"	2120, 4.5, 1550, 6.0, 1070, 0.23		
Dialysable (H ₂ O extr.)	-	-	10 ^{-5.5} - 10 ^{-3.6}	KNO ₃	0.1	6		2570, 4.3, 650, 6.3, 530, 0.34		
Soil	8.6	-	0 - 10 ^{-3.8}	CaCl ₂	0.05	5.5	A _m , K _L	16, 6.0	Dhillon et al. 1981	
	10.0	-	0 - 10 ^{-3.8}	CaCl ₂	0.05	5.5	A _m , K _L	22, 6.3		
	4.2	-	0 - 10 ^{-3.8}	CaCl ₂	0.05	5.5	A _m , K _L	12, 5.2		
	5.6	-	0 - 10 ^{-3.8}	CaCl ₂	0.05	5.5	A _m , K _L	14, 6.0		

Table 11-1 (Contd). ADSORPTION CONSTANTS FOR COPPER

Adsorbent					Adsorbate		Electrolyte			Adsorption Measurements		Reference
Identity (a)			CEC meq/100g	S ₂ A. m ² /g	Conc., M		Identity	Conc., M	pH	Constants (b)	Value (c)	
Soil	Depth	% O.M.										
	0 - 7.5 cm	10.6	18.4	-	10 ^{-5.1} - 10 ^{-3.5}	Simulated sludge	-		6.4	A _m , K _L , K _F , 1/N	(11.2, 7.4), 6.1, 1.0	Sidle and Kardos 1977
	7.5 - 15 cm	5.4	8.4	-	10 ^{-5.1} - 10 ^{-3.5}	leachate	-		5.4	A _m , K _L , K _F , 1/N	(8.8, 6.5), 2.5, 1.0	
	untreated	21.2	57.5	-	0 - 0.005	-	-		5.4	A _m , K _L	175, 3.9	Petrucelli et al. 1978
	H ₂ O ₂ -treated	0	23.7	-	0 - 0.005	-	-		5.4	A _m , K _L	44, 3.6	
	untreated	3.3	38.8	-	0 - 0.005	-	-		6.7	A _m , K _L	136, 3.5	
	H ₂ O ₂ -treated	0	11.3	-	0 - 0.005	-	-		6.7	A _m , K _L	29, 3.0	
	untreated	17.8	22.6	-	0 - 0.005	-	-		7.0	A _m , K _L	148, 4.7	
	H ₂ O ₂ -treated	0	15.4	-	0 - 0.005	-	-		7.0	A _m , K _L	34, 29	
	untreated	3.5	27.5	-	0 - 0.005	-	-		6.0	A _m , K _L	67, 3.7	
	H ₂ O ₂ -treated	0	13.1	-	0 - 0.005	-	-		6.0	A _m , K _L	39, 3.7	
Sediment	Particle size, μm	% O.M.										
	0.44	0.6	-	-	-	-	-	-	-	A _m , K _L	29, -	Ramamoorthy and Rust 1978
	0.007	3.2	-	-	-	-	-	-	-	A _m , K _L	344, 6.0	
	0.16	35.7	-	-	-	-	-	-	-	A _m , K _L	173, 5.2	
	0.40	0.6	-	-	-	-	-	-	-	A _m , K _L	34, 5.1	
	0.27	2.4	-	-	-	-	-	-	-	A _m , K _L	31, 5.1	

(a) O.M. = organic acid

(b) K_F, 1/N = Freundlich constants for A = K_FC^{1/N}; A = μmol g⁻¹; C = μM; A_m = Langmuir adsorption maximum, μmol g⁻¹; K_L = Langmuir constant, log M⁻¹; K_d = distribution coefficient, ml g⁻¹ except Takematsu (1979) and Oakley et al. (1981) values in lg⁻¹; K_{M2}^{M1} = selectivity coefficient; *K_s, *K_s²⁵ = surface complexation constants, log; K_M^{int} = intrinsic adsorption constants, log; K_C = affinity coefficient.

(c) () = estimated values

Section 12

FLUORIDE

Fluoride (F^-) is a negatively charged anion which forms strong complexes with Al^{3+} , an ion which is commonly present in waste leachate or soil under acid conditions. However, the range in pH at which the Al-F complexes are dominant depends upon the F^- activity. Available data suggests that F concentrations in calcareous soils and sediments are controlled by fluorite (CaF_2). Studies of F adsorption/desorption using soils and soil minerals indicate that: 1) fluoride is not strongly adsorbed by soils but the maximum adsorption occurs at pH values of ~4 to 6.5, and 2) fluoride displaces surface-bound OH^- during adsorption. Adequate information is not available to determine whether anions such as SO_4^{2-} , SeO_3^{2-} , and AsO_4^{3-} affect F^- adsorption.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIATION

Fluoride has a -1 valence state. Most known fluoride compounds are fairly soluble. The activity of F^- in soils normally ranges from 10^{-4} to 10^{-10} M (Lindsay 1979). Except in a few cases where soils may contain fluorite and fluorapatite, F^- activities in soils and sediments are expected to be controlled by adsorption/desorption reactions.

To determine the relative abundance of F^- species in ground waters representative of leachates, activities of different F^- species in equilibrium with $F^- = 10^{-5}$ M were plotted using the thermodynamic data (Ball et al. 1980) contained in the geochemical code MINTeq (Felmy et al. 1983). Under the assumed conditions (Figure 12-1), F^- forms very strong complexes with Al^{3+} such that these complexes are dominant below pH values of ~5.5. The pH values below which fluoro complexes of Al^{3+} are dominant decreases with the decrease of F^- activity. At pH values >5.5, F^- is the only dominant species. All of the other F^- complexes with Ca^{2+} , Mg^{2+} , Na^+ , and trace metals (such as Ni^{2+} , Pb^{2+} , Cd^{2+}) do not contribute significantly to the total F in solution.

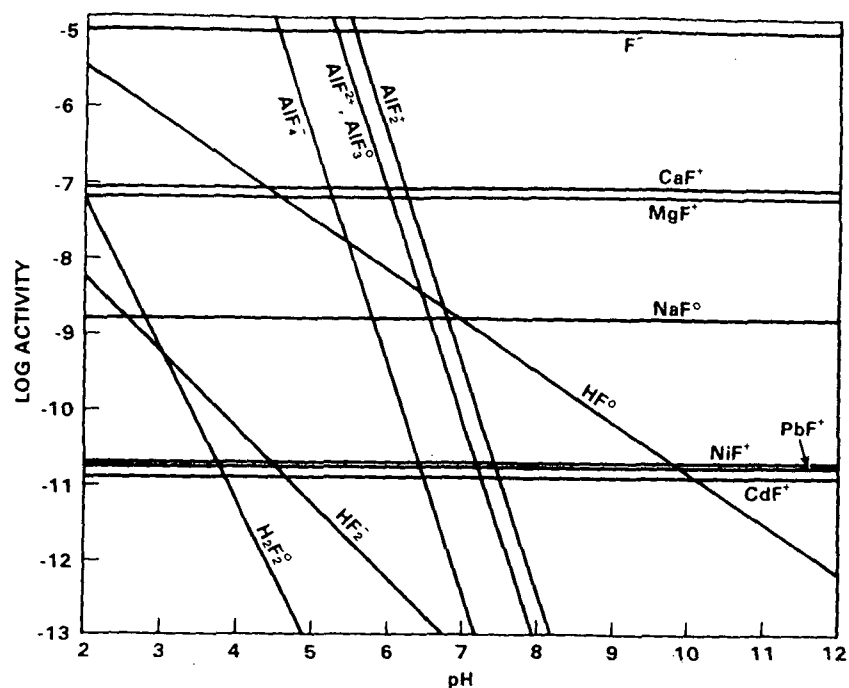


Figure 12-1. Activities of different fluoride species when $F^- = 10^{-5}$, $Na^+ = Ca^{2+} = 10^{-3}$, $Mg^{2+} = 10^{-4}$, $Ni^{2+} = Cd^{2+}$, $Pb^{2+} = 10^{-7}$, and Al^{3+} activity controlled by gibbsite $[Al(OH)_3]$.

PRECIPITATION/DISSOLUTION

Information on observed or predicted solubility-controlling solids of F^- is limited. Nordstrom and Jenne (1977) showed that the solubility of fluorite provides an equilibrium control on dissolved F^- activity in geothermal waters. However, only a small percentage of waters (from Pb and Zn mining areas) were in apparent equilibrium with fluorite, with most being undersaturated (Jenne et al. 1980). In adsorption experiments at $\geq 3.6 \times 10^{-4}$ M fluoride, the results of Chhabra et al. (1980) suggested F precipitation possibly as fluorapatite or fluorite. Other authors (Gupta et al. 1982) have observed high apparent adsorption of F by calcareous soils which they attribute to the possible precipitation of fluorite. Fluoride has strong affinity for Al^{3+} (Figure 12-1) and Semmens and Meggy (1966) indicate that solid phases such as cryolite (Na_3AlF_6) could form through F^- attack on aluminum minerals.

ADSORPTION/DESORPTION

Fluoride adsorption in soil strongly correlates with the content of amorphous Al oxides (Omuetti and Jones 1979). Among a number of soil constituents, including

layer lattice silicates and oxide minerals, $\text{Al}(\text{OH})_3$ appears to have the highest adsorption capacity for F (Bower and Hatcher 1967). Some crystalline aluminosilicates, imogolite, halloysite (Bower and Hatcher 1967), and more probably, amorphous aluminosilicates of volcanic origin (e.g., allophane) have significant adsorption capacity for F as well. While decreasing soil solution pH generally yields greater adsorption of F by soils (Omuetti and Jones 1977, Bower and Hatcher 1967), some calcareous soils may have high apparent adsorption capacities due to precipitation of CaF_2 (Gupta et al. 1982). More commonly, increasing pH and soil sodicity suppresses F adsorption in alkalai soils.

The adsorption behavior of F is strongly influenced by pH (Table 12-1). On goethite, for example, adsorption of F is greatest at a pH (3 to 4) near the pK_a of the anion (Hingston et al. 1968; Hingston et al. 1972) possibly suggesting participation of the protonated species (HF) in the adsorption mechanism. In contrast, maximum F adsorption on chloritized montmorillonite, allophane, and surface soil occur between pH 6 and 7 (Omuetti and Jones 1977). Adsorption of F is negligible above the approximate zero point of charge of goethite and gibbsite (Hingston et al. 1972) indicating that a positively charged surface or the protonated species is required for F retention. The higher F adsorption noted in many acid soils (Omuetti and Jones 1977; Bower and Hatcher 1967) reflects a combination of factors including 1) greater quantities of amorphous Al and Fe oxides, 2) a positive charge distribution on amphoteric hydrous oxides, and 3) the presence of HF . Each of these factors encourages F retention.

The affinity of F for soils is enhanced with increasing ionic strength or in the presence of aqueous monovalent cations of increasing atomic number (Barrow and Shaw 1982). Both these factors contribute to reduce the negative electrostatic charge of the adsorbing surface.

The adsorption mechanism of F on mineral surfaces and soils has not been well defined. Since the fluoride and hydroxyl ions are similar in size, charge, and polarization, it is not surprising that anion or ligand exchange with surface OH^- on clay minerals and hydrous oxides has been proposed as the prominent retention mechanism of F in soil (Hingston et al. 1972; Mott 1981). In fact, most F adsorption studies note an increase in solution pH following adsorption (Perrott et al. 1976). However, some investigators indicate that F adsorption may, in fact, be a chemical reaction lending to displacement of structural OH^- , disruption of the mineral structure, and formation of new surface solid phases such as cryolite (Semmens and Meggy 1966) or soluble fluoroaluminate complexes (Huang and Jackson

1965; Hingston et al. 1972 and Figure 12-1). Though rates of chemical reaction are slower than adsorption, layer lattice silicates appear particularly susceptible to F attack (Semmens and Meggy 1966; Huang and Jackson 1965), while oxide minerals (e.g., gibbsite) are vulnerable under acidic conditions (Hingston et al. 1972). These chemical reactions also lead to formation of hydroxy ions and increase in solution pH (Perrott et al. 1976; Huang and Jackson 1965). Because of its strong affinity for active hydroxyl sites, F has been used in soil testing to detect allophanic (Bonfils 1972) and aluminium-rich (Brydon and Day 1970) soil clays by measurement of evolved OH^- after contact with 1 M NaF.

Table 12-1. ADSORPTION CONSTANTS FOR FLUORIDE

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		References
Identity (a)	CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
Clay Minerals									
Kaolinite	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	6.2	A _m , K _L	21.9, 3.48	Bower and Hatcher 1967
			0 - 10 ^{-2.4}	MgCl ₂	0.01	5.0	A _m , K _L	14.2, 3.56	
Halloysite dehydrated expanded	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	6.1	A _m , K _L	94.0, 3.64	
	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	7.0	A _m , K _L	175, 3.12	
Bentonite	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	8.7	A _m , K _L	trace	
Vermiculite	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	8.5	A _m , K _L	trace	
Alumina									
Freshly ppt'd	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	6.3	A _m , K _L	1820, 4.44	Bower and Hatcher 1967
Coated to bentonite	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	6.3	A _m , K _L	2770, 3.96	
Gibbsite	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	7.0	A _m , K _L	11.7, 3.68	
Fe Oxides									
Goethite	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	7.0	A _m , K _L	trace	Bower and Hatcher 1967
Goethite	-	32	10 ^{-3.7} - 10 ^{-2.5}	NaCl	0.1	3	A _m , K _L	(300, 3.5)	Hingston et al. 1968
			10 ^{-3.7} - 10 ^{-2.5}	NaCl	0.1	4	A _m , K _L	(290, 3.3)	
			10 ^{-3.7} - 10 ^{-2.5}	NaCl	0.1	5	A _m , K _L	(140, 3.3)	
			10 ^{-3.7} - 10 ^{-2.5}	NaCl	0.1	6	A _m , K _L	(70, 3.0)	
Soils									
Sandy loam	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	7.2	A _m , K _L	4.6, 3.48	Bower and Hatcher 1967
			0 - 10 ^{-2.4}	MgCl ₂	0.01	4.8	A _m , K _L	21.0, 2.64	
Silt loam	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	7.7	A _m , K _L	8.1, 3.39	
			0 - 10 ^{-2.4}	MgCl ₂	0.01	3.5	A _m , K _L	20.3, 3.18	
Loam	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	7.3	A _m , K _L	9.0, 3.12	
			0 - 10 ^{-2.4}	MgCl ₂	0.01	4.1	A _m , K _L	13.2, 3.38	
Loam, (dried, rewet)	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	7.3	A _m , K _L	13.8, 2.88	
Clay loam	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	5.6	A _m , K _L	69.3, 3.68	Bower and Hatcher 1967
Clay loam (dried, rewet)	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	5.6	A _m , K _L	99.2, 3.66	
Loam	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	7.9	A _m , K _L	5.8, 3.12	
Clay	-	-	0 - 10 ^{-2.4}	MgCl ₂	0.01	8.0	A _m , K _L	11.3, 3.18	

Table 12-1 (Contd). ADSORPTION CONSTANTS FOR FLUORIDE

Adsorbent			Adsorbate		Electrolyte			Adsorption Measurements		References
Identity (a)		CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
Soils	% Clay	% O.C.	Al, $\mu\text{g/g}$					Soil		
17.8	3.26		1200	10^{-9} - $10^{-2.6}$	NaCl					
21.6	0.52		1300	10^{-9} - $10^{-2.6}$	NaCl		0.1	5.1	A_m, K_L	19.2, 3.620 Muetl and Jones 1977
20.0	0.18		1000	10^{-9} - $10^{-2.6}$	NaCl		0.1	5.6	A_m, K_L	15.0, 3.68
29.0	3.13		1200	10^{-9} - $10^{-2.6}$	NaCl		0.1	5.9	A_m, K_L	9.9, 3.86
39.8	1.39		1900	10^{-9} - $10^{-2.6}$	NaCl		0.1	5.7	A_m, K_L	23.4, 3.61
37.3	0.36		1300	10^{-9} - $10^{-2.6}$	NaCl		0.1	5.5	A_m, K_L	24.7, 3.88
13.9	1.20		1300	10^{-9} - $10^{-2.6}$	NaCl		0.1	6.2	A_m, K_L	16.6, 3.68
43.8	0.53		2300	10^{-9} - $10^{-2.6}$	NaCl		0.1	4.4	A_m, K_L	26.0, 2.86
34.4	0.28		1400	10^{-9} - $10^{-2.6}$	NaCl		0.1	4.8	A_m, K_L	26.7, 3.39
23.7	3.53		1200	10^{-9} - $10^{-2.6}$	NaCl		0.1	5.7	A_m, K_L	21.3, 3.78
25.5	4.31		1200	10^{-9} - $10^{-2.6}$	NaCl		0.1	5.2	A_m, K_L	18.8, 3.61
20.8	2.94		750	10^{-9} - $10^{-2.6}$	NaCl		0.1	6.4	A_m, K_L	32.9, 2.93
27.0	1.99		1000	10^{-9} - $10^{-2.6}$	NaCl		0.1	6.0	A_m, K_L	9.1, 3.50
19.0	0.86		850	10^{-9} - $10^{-2.6}$	NaCl		0.1	6.5	A_m, K_L	19.0, 3.58
19.0	0.79		790	10^{-9} - $10^{-2.6}$	NaCl		0.1	5.6	A_m, K_L	6.9, 3.77
14.9	1.62		900	10^{-9} - $10^{-2.6}$	NaCl		0.1	7.7	A_m, K_L	5.3, 3.10
10.4	0.94		825	10^{-9} - $10^{-2.6}$	NaCl		0.1	5.9	A_m, K_L	10.1, 3.59
18.3	3.03		960	10^{-9} - $10^{-2.6}$	NaCl		0.1	5.9	A_m, K_L	7.8, 3.67
14.8	0.71		1000	10^{-9} - $10^{-2.6}$	NaCl		0.1	5.6	A_m, K_L	14.0, 3.45
14.9	1.18		1300	10^{-9} - $10^{-2.6}$	NaCl		0.1	6.6	A_m, K_L	10.5, 3.44
Na-saturated								4.6	A_m, K_L	27.4, 2.87
Calcareous			-	$0 - 10^{-3.0}$	NaCl		0.1	8.95	A_m, K_L	3.1, 3.66 Gupta et al. 1982
			-	$0 - 10^{-3.0}$	NaCl		0.1	10.4	A_m, K_L	3.8, 3.59
Non-calcareous			-	$0 - 10^{-3.0}$	NaCl		0.1	8.95	A_m, K_L	1.3, 4.16
			-	$0 - 10^{-3.0}$	NaCl		0.1	10.4	A_m, K_L	3.2, 3.52
5% Na-saturated			-	$0 - 10^{-2.6}$	-		-	8.2	A_m, K_L	16.5, 3.64 Chhabra et al. 1979
30% Na-saturated			-	$0 - 10^{-2.6}$	-		-	9.45	A_m, K_L	18.5, 3.41
70% Na-saturated			-	$0 - 10^{-2.6}$	-		-	9.95	A_m, K_L	4.5, 3.87

(a) O.C = organic carbon

(b) A_m = Langmuir adsorption maximum, $\mu\text{mol g}^{-1}$

K_L = Langmuir constant, $\log M^{-1}$

(c) () = estimated values

Section 13

IRON

Both Fe(II) and Fe(III) oxidation states are stable under aqueous environmental pH and redox conditions. Fe(III) species are dominant under oxidizing conditions and Fe(II) species under reducing conditions. Iron concentrations in aqueous environments are expected to be controlled by precipitation/dissolution reactions. Metastable ferrosic hydroxide $[\text{Fe}_3(\text{OH})_8]$, which persists in changing redox conditions is shown to control maximum Fe concentrations for a wide range in redox conditions ($\text{pe} + \text{pH} > 8$). Other iron oxides and hydroxides less soluble than $\text{Fe}_3(\text{OH})_8$ have also been reported to be solubility-controlling. Adsorption can be an important retention mechanism of iron at low pH or at low aqueous concentrations.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIES

Iron in geologic environments exists in the +2 and +3 oxidation states which are stable over a broad range of pH and redox conditions. Redox potential strongly affects both the stable solid and solution species. Under oxidizing conditions, Fe(III) minerals are more stable than Fe(II) minerals. Based on available thermodynamic data, Lindsay (1979) has determined the relative stability of Fe oxides. His calculations show that under oxidizing conditions ($\text{pe} + \text{pH} > 11.5$) soil $\text{Fe}(\text{OH})_3$ (intermediate in solubility to amorphous hydroxide and crystalline oxide) controls the solubility; below $\text{pe} + \text{pH}$ of 11.5, magnetite (Fe_3O_4) is the stable phase until siderite (FeCO_3) forms [$\text{pe} + \text{pH} 3.7$ for $\text{CO}_2(\text{g}) < 10^{-1.5}$ atmospheres].

To determine the relative abundance of Fe(II) and Fe(III) species in ground waters representative of utility waste leachates and to show the effect of redox potential on the solubility of Fe(III) solids, activities of different Fe species in equilibrium with $\text{Fe}(\text{OH})_3(\text{a})$ at two different redox conditions were plotted using the thermodynamic data (Ball et al. 1980) contained in the geochemical model MINTEQA (Felmy et al. 1983). Under relatively oxidizing conditions ($\text{pe} + \text{pH} = 16$) and for high F^- (10^{-4} M) waters, fluoro complexes of Fe(III) are the dominant aqueous species at pH values of approximately < 4.2 (Figure 13-1). At high pH values, hydrolysis species of Fe(III) [$\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_4^-$] are dominant. Under these

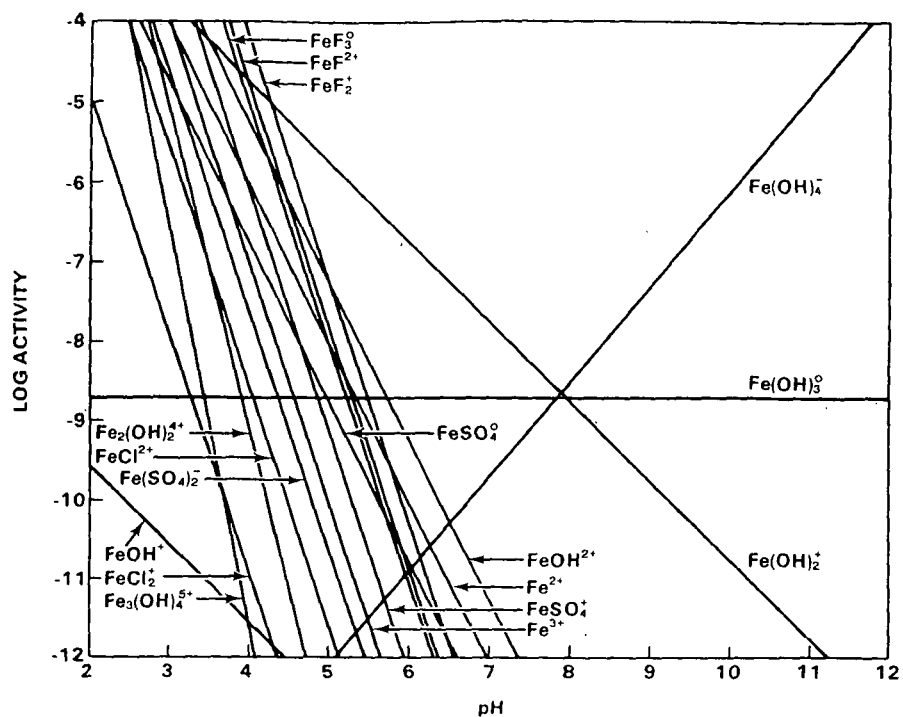


Figure 13-1. Activities of different iron species in equilibrium with $\text{Fe}(\text{OH})_3(\text{a})$ under relatively oxidizing conditions ($\text{pe} + \text{pH} = 16$), when activities of $\text{SO}_4^{2-} = \text{Cl}^- = 10^{-3}$, $\text{F}^- = 10^{-4}$.

conditions (Figure 13-1), the Fe(II) species and Fe(III) complexes with SO_4^{2-} and Cl^- do not contribute significantly to the total Fe in solution. Decreasing the redox potential ($\text{pe} + \text{pH} = 7$) increases the total Fe in solution and changes the dominant aqueous species (Figure 13-2). Fe^{2+} is the dominant aqueous species at pH values < 9.2 , and species other than FeSO_4^0 do not contribute significantly to the total Fe.

Figures 13-1 and 13-2 show that with the decrease in redox ($\text{pe} + \text{pH}$) potential, $\text{Fe}(\text{OH})_3(\text{a})$ becomes very soluble, and as mentioned earlier, Fe_3O_4 instead of $\text{Fe}(\text{OH})_3(\text{a})$ would be the stable compound.

PRECIPITATION/DISSOLUTION

Iron forms several sparingly soluble solids under different redox conditions, and it is generally accepted that Fe concentrations in ground waters are primarily controlled by precipitation/dissolution reactions. Back and Barnes (1965) measured solution concentrations of Fe^{2+} as a function of redox potential and pH in ground waters. Their data suggest the presence of ferrosic hydroxide [$\text{Fe}_3(\text{OH})_8(\text{s})$] in many ground waters. Equilibrium with iron oxides was also implicated by Barnes and Back

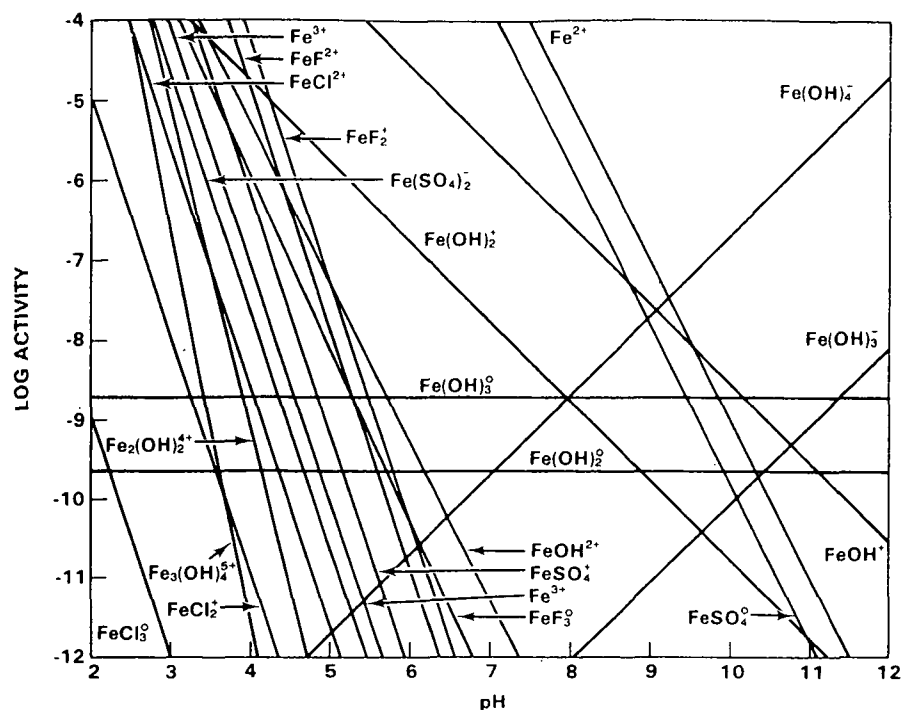


Figure 13-2. Activities of different iron species in equilibrium with $\text{Fe}(\text{OH})_3(\text{a})$ under relatively reducing conditions ($\text{pe} + \text{pH} = 7$), when activities of $\text{SO}_4^{2-} = \text{Cl}^- = 10^{-3}$, $\text{F}^- = 10^{-4}$.

(1964) over a wide range of pH and redox potentials. Helz and Sinex (1974) measured dissolved iron, pH, and redox potential in thermal springs and found that $\text{Fe}_3(\text{OH})_8(\text{s})$ may be controlling Fe solubility. Other authors have also suggested that $\text{Fe}_3(\text{OH})_8$ may be important in controlling Fe^{2+} levels (Schwab and Lindsay 1983; Ponnampetuma et al. 1967; Pasricha and Ponnampetuma 1976). Schwab and Lindsay (1983) presented convincing evidence that indicates maximum iron concentrations, over a wide range of redox potentials, are controlled by ferrosic hydroxide and siderite (FeCO_3); ferrosic hydroxide was found to control concentrations at $\text{pe} + \text{pH} > 8$ and siderite at $\text{pe} + \text{pH} < 8$. Schwab and Lindsay (1983) point out that ferrosic hydroxide is metastable and is expected to persist in changing redox environments. They also state that under stable redox conditions, less soluble iron oxides can control Fe concentrations.

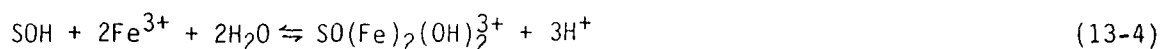
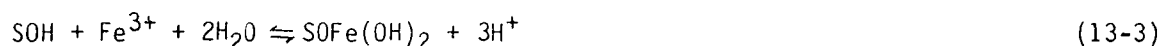
ADSORPTION/DESORPTION

The behavior and attenuation of Fe in soil and subsoil is controlled, to a large extent, by precipitation reactions leading to formation of amorphous and crystalline secondary minerals. These reactions and the identity of secondary Fe solid phases

have been investigated in detail (e.g., Oades 1968; Bingham et al. 1978). Secondary Fe hydrous oxides are important soil/subsoil adsorbents of anionic (Davis and Leckie 1980) and cationic metallic constituents (Jenne 1968) in utility waste leachate.

Iron(III) is strongly adsorbed, or actually complexed, by soil humic acid at pH <3 (Kerndorff and Schnitzer 1980). The affinity of soil organic matter for Fe(III) is greater than for any other metal except Hg(II) and Cu(II) (Kerndorff and Schnitzer 1980). Thus, the distribution of extractable Fe in soil is strongly influenced by organic matter (Wada and Gunjigake 1979). Other soil constituents which adsorb Fe(III) are crystalline oxides (Schindler et al. 1976; James and Healy 1972a, 1972b; Stumm et al. 1976; O'Melia and Stumm 1967), clay minerals (Page and Whittig 1961; Rengasamy and Oades 1977; Fordham 1969), and hydrous oxides of Fe and Mn (Wada and Gunjigake 1979). The adsorption of Fe(II), the primary valence state under reducing conditions, has not been studied in any degree of detail.

The adsorption of Fe(III) on silica (Schindler et al. 1976, James and Healy 1972a) and clay minerals (Fordham 1969) is strongly pH dependent (Table 13-1). The adsorption edge of Fe(III) on silica occurs almost three pH units below that of Pb and Cu, two strongly adsorbing trace metals (Schindler et al. 1976; James and Healy 1972a). The pH of the adsorption edge for each metal qualitatively correlates with the value of the first hydrolysis constant. At pH values below 3, the adsorption of Fe(III) by clay minerals (Fordham 1969; Page and Whittig 1961) and silica (Schindler et al. 1976) is accompanied by the release of 1.0 to 1.2 protons for each Fe ion adsorbed. Adsorption may occur through surface complexation.



Reactions 13-3 and 13-4 can occur only at low concentrations of Fe(III) ($\sim 10^{-8}$ M) when pH is >6. Above pH 2, FeOH^{2+} is likely the dominant adsorbing species.

The effects of competing cationic elements and soluble ligands on Fe adsorption is poorly documented; however, the adsorption of Fe(III) by clay minerals is unaffected by the presence of NO_3^- , SO_4^{2-} , or Cl^- (Page and Whittig 1961). Water soluble organic

ligands (e.g., fulvic acids) may form strong aqueous complexes with Fe(III) (Perdue et al. 1976; Schnitzer 1969), maintaining solution concentrations at far higher levels than that predicted by solubility considerations alone. These complexes will, in general, increase iron mobility through soil/land/subsoil systems. They may, however, be adsorbed by certain mineral constituents (Dawson et al. 1978).

Autoradiography and electron microscopy reveal that at low aqueous concentrations of Fe(III) specific adsorption occurs on clay minerals at the particle edges where exposed Al-OH groups exist (Fordham 1973). Increased solution concentrations induce precipitation of an evenly distributed coating of Fe(III)-oxides on the clay surfaces, beginning at the particle edges.

Table 13-1. ADSORPTION CONSTANTS FOR IRON

Adsorbent			Adsorbate		Electrolyte		Adsorption Measurements		Reference
Identity	CEC meq/100g	S _A , m ² /g	Conc., M	Identity	Conc., M	pH	Constants (a)	Value (b)	
<u>Clay Minerals</u>									
Kaolinite	-	15	10 ^{-5.5} - 10 ⁻⁵	CaCl ₂	0.05	3	A _m , K _L	(4.3, 5.5)	Fordham 1969
Ca-saturated	-		10 ^{-5.5} - 10 ⁻⁵	CaCl ₂	0.05	4	"	(14.9, 6.0)	
Bentonite, Na-form	-	-	0 - 0.015	-	-	3	A _m , K _L	(6180, 2.8)	Rengasamy and Oades 1977
Illite, Na-form	-	-	0 - 0.015	-	-	"	"	(4920, 2.9)	
Kaolinite, Na-form	-	-	0 - 0.015	-	-	"	"	(1430, 2.6)	
Montmorillonite	-	-	10 ^{-2.5}	-	-	>0.5	A	220	Page and Whittig 1961
Na-form	-	-	10 ^{-2.5}	-	-	>1.0	A	260	
						>1.6	A	280	
						>2.1	A	280	
H-form	-	-	10 ^{-2.5} - 10 ^{-2.2}	-	-	-	A _m , K _L	(460, 4.2)	
<u>Silica</u>									
SiO ₂	-	372	-	NaClO ₄	3.0	0-5	*K ₁ ^S SiOFe *K ₂ ^S (SiO) ₂ Fe	-1.77 ± 0.04 -4.22 ± 9.95	Schindler et al. 1976
SiO ₂	-	-	-	NaClO ₄	3.0	-	K _{Fe} ^{int} , K _{int} ^{int} , K _{FeOH}	(5.4, 6.0)	Stumm et al. 1976
SiO ₂	-	5	10 ^{-3.9}	-	-	2.7	A	(4.0)	James and Healy 1972a
SiO ₂	-	5	10 ^{-3.9}	-	-	1.5- 3.0	ΔG _{chem} ^o	-8.5	James and Healy 1972b

Table 13-1 (Contd). ADSORPTION CONSTANTS FOR IRON

Adsorbent			Adsorbate	Electrolyte		Adsorption Measurements		Reference
Identity	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (a)	Value (b)
<u>Silica</u>								
SiO ₂	-	5	10 ^{-3.9}	-	-	1.5-3.0	*K _{Fe} ^{Int}	-2.2
							*K _{FeOH} ^{Int}	-4.0
							*K _{Fe(OH)₂} ^{Int}	-5.1
							*K _{Fe₂(OH)₂} ^{Int}	-11.9
							K _{Fe} ^{Int}	(5.0)
							K _{FeOH} ^{Int}	(6.2)
SiO ₂	-	2.06	0 - 10 ^{-3.4}	-	-	2.5-3.0	A _m , K _L	(0.5, 6.4)
							A _m , K _L	(1.0, 6.7)
<u>Organic Matter</u>								
Humic acid (soil)	-	-	10 ^{-4.3} - 10 ^{-3.3}	-	-	2.4	A _m , K _L	(1760, 3.2)
<u>Soil</u>								
Clay	51	9	51.3 10 ^{-2.7}	municipal waste leachate	-	5.4	PV, CL	(4.5, 2.0)
Silty clay loam	31	19	61.5 10 ^{-2.7}			5.4	PV, CL	(6.5, 3.4)
Sandy loam	15	6	19.5 10 ^{-2.7}			5.4	PV, CL	(4.3, 1.3)
Sandy loam	11	10	38.3 10 ^{-2.7}			5.4	PV, CL	(4.3, 1.5)
Sand	8	10	8.9 10 ^{-2.7}			5.4	PV, CL	(1.5, 0.2)
Sand	4	2	8.0 10 ^{-2.7}			5.4	PV, CL	(1.0, 0)

(a) A_m = Langmuir adsorption maximum, $\mu\text{mol g}^{-1}$ K_L = Langmuir constant, $\log \text{M}^{-1}$ A = adsorption, $\mu\text{mol g}^{-1}$ *K₁^S, *K₂^S = surface complexation constants for ionic species, \log K_M^{Int} = intrinsic adsorption constant for ionic species, \log Δ_{chem}^{*} = free energy of adsorption, $k_{\text{end}} \text{mol}^{-1}$

PV = pore volumes to 50% breakthrough

CL = column loading, $\mu\text{mol g}^{-1}$

(b) () = estimated values

Section 14

LEAD

In natural aqueous environments, lead (Pb) primarily exists as Pb(II). The dominant aqueous species are Pb^{2+} in acidic conditions and Pb^{2+} -carbonate complexes in alkaline conditions. Both precipitation/dissolution and adsorption/desorption appear to control Pb concentrations. Lead-phosphates in noncalcareous sediments and PbCO_3 in calcareous and alkaline soils sediments have been reported to be solubility- controlling solids. Iron and Mn oxides are strong specific adsorbents for Pb. In addition to specific adsorption, Pb retention also occurs through ion exchange. Except at high Pb concentrations where ion exchange predominates, competing ions appear to have little effect on Pb adsorption. Information is not currently available to determine if Pb adsorption in subsoil/substrata is significantly modified by other solutes present in utility waste leachate.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIES

Naturally occurring lead (Pb) has three oxidation states: 0 (metal), Pb(II), and Pb(IV). In ground waters, Pb primarily exists as Pb(II); it exists as Pb(IV) only in extremely oxidizing conditions, outside the environmental pH and Eh range. In addition, solid compounds of Pb(IV) will not form under environmental conditions (Lindsay 1979). Some of the Pb(II) compounds with relatively low solubility include Pb-carbonates [PbCO_3 , $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$] and Pb-phosphates as well Pb-phosphates-halides [$\text{Pb}_3(\text{PO}_4)_2$, $\text{Pb}_5(\text{PO}_4)_3\text{Br}$, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$] (Lindsay 1979).

To determine the relative abundance of Pb(II) species in ground waters representative of leachates, activities of different Pb species (Pb^{2+} fixed at 10^{-7} M or controlled by cerussite) were plotted (Figure 14-1) using the thermodynamic data (Truesdell and Jones 1974; Ball et al. 1980) contained in the geochemical model MINTEQ (Felmy et al. 1983). Under the assumed conditions (Figure 14-1), Pb^{2+} followed by PbSO_4^0 is the dominant aqueous species in ground waters of pH values ≤ 7 . At pH values ≥ 7 , Pb-carbonate complexes are dominant. With the exception of PbCl^+ which contributes approximately 8% to the total soluble Pb at pH values ≤ 7 , other Pb complexes with Br^- , F^- , NO_3^- , I^- , and OH^- do not contribute significantly to the total Pb in solution.

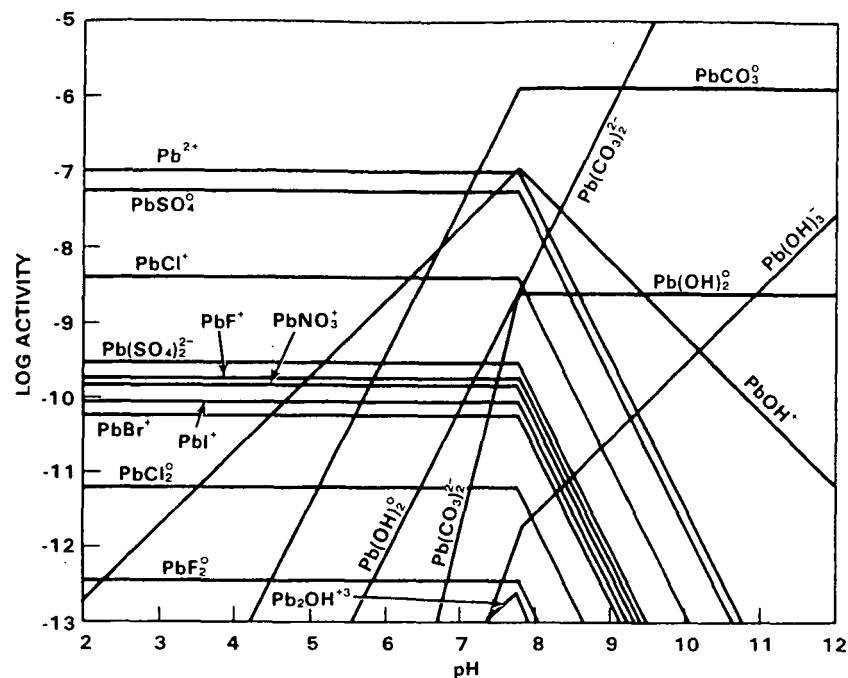


Figure 14-1. Activities of different Pb(II) species when activity of Pb^{2+} is fixed at 10^{-7} or controlled by cerussite ($PbCO_3$), $SO_4^{2-} = Cl^- = 10^{-3}$, $Mg^{2+} = NO_3^- = 10^{-4}$, $Br^- = I^- = 10^{-5}$ and $CO_2(gas) = 10^{-3.52}$ atmospheres.

PRECIPITATION/DISSOLUTION

Nriagu (1974) pointed out that Pb phosphates can readily precipitate and could be a major factor in the biochemistry of Pb. However, no direct identification of Pb phosphate precipitates in natural aqueous systems has been made. Santillan-Medrano and Jurinak (1975) studied the chemistry of Pb in soils and concluded that the solution concentrations of Pb appear to be regulated by solid phases that include phosphates. Several Pb compounds [$Pb(OH)_2$, $Pb_3(PO_4)_2$, $Pb_4O(PO_4)_2$, $Pb_5(PO_4)_3OH$], depending upon pH, appeared to be controlling the solubility of lead in noncalcareous soils. Depending on the pH, $PbCO_3$ was found to be the controlling phase in calcareous soils. Jenne et al. (1980) also reported that $PbCO_3$ appeared to control the Pb concentrations in a few water samples from the Missouri tri-state mining area.

Most of the researchers studying Pb adsorption used fairly high concentrations of Pb, but only a few made an attempt at estimating whether precipitation of Pb solids could be controlling Pb concentrations. However, $Pb(OH)_2$ was indirectly shown to be the solubility-controlling solid phase in several experiments (Abd-Elfattah and Wada 1981; Lagerwerff and Brower 1973; Singh and Sekhon 1977a). For example, lead

carbonate was found to be the solubility-controlling solid in pH 6 leachates spiked with Pb (Griffin and Shimp 1976). Hem (1977) states that lead carbonate and basic lead carbonates are potential controls for Pb solubility, especially in alkaline environments. Laboratory tests conducted with solutions of pH 8.6 spiked to 2070 ppm Pb showed that equilibrium lead concentrations were only 2 ppm. Because the predicted Pb concentrations (13 ppm) in equilibrium with Pb hydroxy carbonate were similar to the observed value, Hem (1977) concluded that lead hydroxy carbonate was the controlling phase. Soldatini et al. (1976) also postulated the formation of Pb carbonate in alkaline and calcareous soils spiked with $10^{-4.4}$ to 10^{-6} M Pb.

ADSORPTION/DESORPTION

Lead is strongly retained by soils and model adsorbents, by ion exchange and specific adsorption. The soil properties which most often correlate with Pb adsorption are soil organic matter and clay content (Singh and Sekhon 1977a; Soldatini et al. 1976; Riffaldi et al. 1976; Abd-Elfattah and Wada 1981), but studies with model adsorbents clearly demonstrate the importance of Mn and Fe oxides (Gadde and Laitinen 1974; McKenzie 1980). Although their apparent binding energies (Langmuir K) do not vary appreciably, the adsorption capacity of individual soil constituents decrease in the following order Mn oxides*, Fe oxides**, Organic Matter***, and clay minerals.†

The adsorption of Pb is strongly pH dependent (Table 14-1) on sediments (Salim and Cooksey 1980; Brown 1979) Fe oxides (Balistrieri and Murray 1982; Forbes et al. 1976; McKenzie 1980; Gadde and Laitinen 1974; Benjamin and Leckie 1981) Al oxides (Davis and Leckie 1978; Hohl and Stumm 1976) clay minerals (Griffin and Shimp 1976) and organic material (Bunzl et al. 1976). Under comparable experimental conditions, lead adsorption is high and less pH dependent on Mn oxides (McKenzie 1980; Gadde and Laitinen 1974). The Pb adsorption edge occurs at lower pH than that of Cu and Zn on amorphous iron oxyhydroxide (Benjamin and Leckie 1981), hematite (McKenzie 1980), and γ -FeOOH and γ -Al₂O₃ (Benjamin and Leckie 1980) suggesting stronger adsorption of Pb. The exact cause for pH-dependent adsorption on hydrous oxides is difficult to verify because both the properties of the oxide surface (charge and potential) and solution composition (metal ion speciation) change with pH. Hence, the rise in adsorption with increasing pH has been ascribed to various factors by different

* McKenzie 1980; Gadde and Laitinen 1974.

** Balistrieri and Murray 1982; Forbes et al. 1976; McKenzie 1980; Gadde and Laitinen 1974.

*** Bunzl et al. 1976; Bunzl 1974a and 1974b; Kerndorff and Schnitzer 1980.

† Bittell and Miller 1974; Griffin and Au 1977; Griffin and Shimp 1976.

investigators including: adsorption of the hydrolytic complex PbOH^+ (Davis and Leckie 1978), adsorption of Pb^{2+} with decreasing surface positive charge (Barrow et al. 1981), and formation of bidentate surface complexes with Pb^{2+} (Hohl and Stumm 1976).

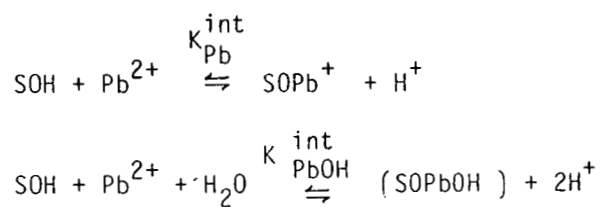
The effects of competing ions on Pb adsorption (Table 14-1) is strongly dependent on whether Pb solution concentrations exceed the specific adsorption capacity of soil/subsoil or an individual adsorbent. The specific adsorption of Pb on oxides of Mn (Gadde and Laitinen 1973; Gadde and Laitinen 1974), amorphous Fe oxyhydroxide (Benjamin and Leckie 1981) and goethite (Balistreri and Murray 1982) is relatively unaffected by other metallic cations (Cu, Zn, and Cd) in equal concentration. However, high concentrations of certain divalent cations (e.g., Mg^{2+} at 10^{-2} M) may, due to their weak specific adsorption, decrease Pb adsorption to Fe oxides (Balistreri and Murray 1982). Increasing ionic strength with NaCl, NaClO_4 or NaNO_3 has little effect on Pb adsorption by Fe oxides (Balistreri and Murray 1982; Swallow et al. 1980). Under conditions where cation exchange is the prominent adsorption mechanism, such as on clays or in soil at higher Pb concentration (e.g., 10^{-4} M), the presence of metal (e.g., Al, Fe) and alkaline earth (Ca, Mg) cations reduces Pb adsorption through exchange mass action (Griffin and Au 1977; Griffin and Shimp 1976; Soldatini et al. 1976; Riffaldi et al. 1976; Lagerwerff and Brower 1973). Exchange selectivity coefficients indicate Pb is more strongly bound than Ca or Al (Lagerwerff and Brower 1973; Bittell and Miller 1974).

The influence of complexing ligands on Pb adsorption has not been studied in detail. The adsorption of Pb on amorphous Fe oxyhydroxide is unaffected by ClO_4^- , but is reduced at higher concentrations of Cl^- (10^{-1} M) by formation of di- and tri-chloro solution complexes (Swallow et al. 1980). In two separate instances, Cl^- has been observed to have no effect (Balistreri and Murray 1982) and to increase Pb adsorption on goethite by formation and adsorption of PbCl^- complexes (Barrow et al. 1981). Nitrate has no effect on Pb adsorption by goethite while SO_4^{2-} (10^{-2} M) increases adsorption, possibly by decreasing positive charge through specific adsorption (Balistreri and Murray 1982). Limited evidence suggests that organically complexed Pb (e.g., by humic acids) may be adsorbed by clay minerals (Griffin and Shimp 1976; Hatton and Pickering 1980).

The adsorption of Pb on soils and sediments (Singh and Sekhon 1977a; Soldatini et al. 1976; Riffaldi et al. 1976; Ramamoorthy and Rust 1978) and clay minerals (Griffin and Shimp 1976) at constant pH, often conforms to the Langmuir isotherm over a narrow range in Pb concentration. When exchange-adsorption is the prominent

mechanism, selectivity coefficient (Abd-Elfatta and Wada 1981; Bittell and Miller 1974; Lagerwerff and Brower 1973) or the competitive Langmuir equation (Griffin and Au 1977) apply if competing cationic solutes are present. At higher concentrations of Pb, both specific and nonspecific multiple adsorption sites become important and the Freundlich equation best describes the adsorption data (Soldatini et al. 1976; Riffaldi et al. 1976; Salim and Cooksey 1980).

The pH-dependent adsorption of Pb on a number of amphoteric oxides, hydrous oxides, and a sediment has been simulated using electrostatic adsorption models. The adsorption of Pb by silica (Schindler et al. 1976; Davis and Leckie 1978), aluminum oxide (Hohl and Stumm 1976; Davis and Leckie 1978), and iron oxides (Davis and Leckie 1978; Balistrieri and Murray 1982) can be accurately described using a surface complexation model in which Pb^{2+} and PbOH^+ replace protons on surface hydroxyl groups, i.e.,



Others suggest that only Pb^{2+} (e.g., Hohl and Stumm 1976; Barrow et al. 1981) and select solution species (e.g., PbCl^+) (Barrow et al. 1981) participate in surface complexation reactions. It is possible through careful control of experimental conditions and extensive measurements to describe the pH-dependent adsorption of Pb by a heterogeneous mineral matrix (sediment) using an electrostatic adsorption model (Brown 1979).

Table 14-1. ADSORPTION CONSTANTS FOR LEAD

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		Reference
Identity ^(a)	CEC	S.A.	Conc., M	Identity	Conc., M	pH	Constants ^(b)		Value ^(c)
	meq/100g	m ² /g							
Clay Minerals									
Montmorillonite	100.8	-	-	Cl ⁻	10 ⁻³	-	K ^{Pb} _{Ca}	0.60	Bittell and Miller 1974
Montmorillonite	-	-	0-0.0125	Ca(ClO ₄) ₂	0.1	5.0	A _m , K _L	(440, 3.1-3.4)	Griffin and Au 1977
Montmorillonite	-	-	10 ^{-4.3} - 10 ^{-2.7}	Landfill leachate	~0.1	5.0	A ^I _m , K ^I _L	8.8, (4.3)	Griffin and Shimp 1976
							A ^{II} _m , K ^{II} _L	5.38, (2.1)	
	-	-	10 ^{-4.3} - 10 ^{-2.7}	-	-	5.0	A _m	398	
Kaolinite	2.2	-	-	Cl ⁻	10 ^{-3.6}	-	K ^{Pb} _{Ca}	0.34	Bittell and Miller 1974
Kaolinite	-	-	10 ^{-4.3} - 10 ^{-2.7}	-	-	5.0	A _m	76.8	Griffin and Shimp 1976
	-	-	10 ^{-4.3} - 10 ^{-2.7}	NaCl	0.1	5.0	A _m	49.4	
	-	-	10 ^{-4.3} - 10 ^{-2.7}	Landfill leachate	~0.1	5.0	A ^I _m , K ^I _L A ^{II} _m , K ^{II} _L	8.1, (4.1) 41.2, (3.0)	
	-	-	10 ^{-4.3} - 10 ^{-2.7}	Landfill leachate	~0.4	5.0	A ^I _m , K ^I _L A ^{II} _m , K ^{II} _L	4.8, (4.1) 11.6, (3.5)	
Illite	15.4	-	-	Cl ⁻	10 ⁻³	-	K ^{Pb} _{Ca}	0.44	Bittell and Miller 1974
Silica									
SiO ₂	-	160	-	-	-	4-7	*K ^S ₁ SiOPb *K ^S ₂ (SiO) ₂ Pb	-5.09 -10.68	Schindler et al. 1976
SiO ₂	-	-	-	-	-	-	K ^{Int} _{Pb} , K ^{Int} _{PbOH}	(2.1, 4.2)	Stumm et al. 1976.

Table 14-1 (Contd). ADSORPTION CONSTANTS FOR LEAD

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		Reference
Identity (a)	CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
<u>Silica</u>									
α -SiO ₂	-	-	10 ^{-6.3}	-	-	-	K _{Pb} ^{Int} K _{Pb} ^{Int} K _{PbOH}	4.6, 7.8	Davis and Leckie 1978
<u>Alumina</u>									
γ -Al ₂ O ₃	-	117	10 ⁻⁴ - 10 ^{-3.5}	NaClO ₄	0.1	4-7	*K ₁ ^S AlOPb	-2.2	Hohl and Stumm 1976
							*K ₂ ^S (AlO) ₂ Pb	-8.1	
							K _{Pb} ^{Int} K _{PbOH} ^{Int}	(7.3, 9.1)	
γ -Al ₂ O ₃	-	-	10 ^{-3.5}	-	-	-	"	6.4, 8.9	Davis and Leckie 1978
			10 ^{-4.3}	-	-	-	"	- , 8.7	
			10 ^{-6.3}	-	-	-	"	6.4, 10.2	
<u>Fe Oxides</u>									
Goethite (α -FeOOH)	-	51.8	10 ^{-7.1} - 10 ^{-4.6}	Seawater	~0.7	3-7	*K _{Pb} ^{Int} K _{Pb} ^{Int} *K _{PbOH}	-1.8, -5.0	Bailstrieri and Murray 1982
							K _{Pb} ^{Int} K _{PbOH} ^{Int}	(8.6, 11.7)	
Goethite	-	89	10 ^{-4.5}	NaNO ₃	0.08	4-6	K _C ^I	-2.0	Forbes et al. 1976
Goethite	-	75	10 ⁻³ - 10 ^{-2.2}	KNO ₃	0.1	5.0	A _m , K _L	(85, 2.9)	McKenzie 1980
Hematite (α -Fe ₂ O ₃)	-	20	10 ⁻³ - 10 ^{-2.2}	KNO ₃	0.1	5.0	A _m , K _L	(56, 3.2)	McKenzie 1980

Table 14-1 (Contd). ADSORPTION CONSTANTS FOR LEAD

Adsorbent			Adsorbate		Electrolyte			Adsorption Measurements		Reference
Identity (a)	CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)		
<u>Fe Oxides (contd)</u>										
Amorphous Fe ₂ O ₃ ·H ₂ O	-	-	10 ^{-3.3} - 10 ^{-2.6}	-	-	-	-	-		
aged 24 hr						5	A _m , K _L	(2000, 28)	Gadde and Laitinen 1973	
fresh						6	A _m , K _L	(2400, 4.9)		
coprecipitation						6	A _m , K _L	(3700, 4.5)		
aged 24 hr						6	A _m , K _L	(2400, 4.10)		
aged 24 hr						6	A _m , K _L	(2700, 3.9)		
Amorphous Fe ₂ O ₃ ·H ₂ O	-	-	10 ^{-6.3}	-	-	-	K _{Pb} ^{Int} K _{PbOH} ^{Int}	6.9, 11.1	Davis and Leckie 1978	
<u>Mn Oxides</u>										
Hydrous Mn oxide	-	-	10 ^{-3.5} - 10 ^{-2.8}	-	-	6	A _m , K _L	(7000, 3.7)	Gadde and Laitinen 1974	
δ-MnO ₂	-	98	10 ⁻³ - 10 ^{-2.2}	KNO ₃	0.1	5	A _m , K _L	(2600, 4.0)		
α-MnO ₂ (K ₂ Mn ₈ O ₁₆)	-	206	10 ⁻³ - 10 ^{-2.2}	KNO ₃	0.1	5	A _m , K _L	(2700, 3.8)		
<u>II Oxide</u>										
	-	-	-	NaClO ₄	1.0		*K ₁ ^S , SiOPb, *B ₂ ^S (SiO) ₂ Pb	-5.1, -10.7	Stumm et al. 1976	
							K _{Pb} ^{Int} , K _{PbOH} ^{Int}	(8.0, 13.5)		
<u>Organic Matter</u>										
Peat	-	-	10 ^{-4.6} - 10 ^{-3.6}	-	-	~4	A _m , K _L	(300-500, 3.7-5.3)	Bunzl 1974a, 1974b	
Humic Acid	-	-	10 ^{-4.6} - 10 ^{-3.6}	-	-	~4	A _m , K _L	(560, 3.6)		
Humic acid	-	-	10 ^{-4.3} - 10 ^{-3.3}	-	-	2.4	A _m , K _L	(52, 4.2)	Kerndorff and Schnitzer 1980	

Table 14-1 (Contd). ADSORPTION CONSTANTS FOR LEAD

Adsorbent				Adsorbate		Electrolyte			Adsorption Measurements		Reference
Identity (a)			CEC meq/100g	S ₂ A. m/g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
Soil	% Clay	% O.C.									
10.1	0.61	6.96	-	10 ^{-4.6}	10 ^{-3.3}	KCl	0.1	7	A _m , K _L	7.0, 3.9	Singh and Sekhon 1977
31.2	1.26	18.2	-	10 ^{-4.6}	10 ^{-3.3}	KCl	0.1	7	A _m , K _L	23, 4.9	
10.4	0.69	6.09	-	10 ^{-4.6}	10 ^{-3.3}	KCl	0.1	7	A _m , K _L	11.5, 3.8	
24.6	0.75	12.18	-	10 ^{-4.6}	10 ^{-3.3}	KCl	0.1	7	A _m , K _L	16.5, 4.5	
20.2	0.76	10.44	-	10 ^{-4.6}	10 ^{-3.3}	KCl	0.1	7	A _m , K _L	11.5, 4.3	
5.5	0.33	3.83	-	10 ^{-4.6}	10 ^{-3.3}	KCl	0.1	7	A _m , K _L	8.5, 3.7	
8.9	0.34	4.35	-	10 ^{-4.6}	10 ^{-3.3}	KCl	0.1	7	A _m , K _L	10.5, 3.7	
6.8	7.8	32.5	-	10 ⁻⁶	10 ^{-4.4}	-	-	7.7	A _m , K _L , K _F , 1/N	180, 4.2, 57.4, 0.15	Soldatini et al. 1976 Riffaldi et al. 1976
						CaCl ₂	0.05	7.7	A _m , K _L , K _F , 1/N	112, 4.7, 12.6, 0.33	
4.0	0.9	8.8	-	10 ⁻⁶	10 ^{-4.4}	-	-	8.2	A _m , K _L , K _F , 1/N	42, 4.2, 14.4, 0.14	
						CaCl ₂	0.05	8.2	A _m , K _L , K _F , 1/N	16.5, 4.7, 4.3, 0.22	
6.6	4.2	20.0	-	10 ⁻⁶	10 ^{-4.4}	-	-	7.9	A _m , K _L , K _F , 1/N	122, 4.4, 43.6, 0.14	
						CaCl ₂	0.05	7.9	A _m , K _L , K _F , 1/N	70, 4.6, 16.6, 0.21	

Table 14-1 (Contd). ADSORPTION CONSTANTS FOR LEAD

Adsorbent				Adsorbate		Electrolyte			Adsorption Measurements		Reference
Identity (a)		CEC meq/100g	$S_d A_s$ m ² /g	Conc., M		Identity	Conc., M	pH	Constants (b)	Value (c)	
Soil	% Clay	% O.M.									
	7.6	2.1	16.2	-	$10^{-6} - 10^{-4.4}$	-	-	8.3	A_m, K_L $K_F, 1/N$	78, 4.5 30.1, 0.13	Soldatini et al. 1976 Riffaldi et al. 1976
						$CaCl_2$	0.05	8.3	A_m, K_L $K_F, 1/N$	43, 4.3, 5.6, 0.27	
	23.1	4.4	31.2	-	$10^{-6} - 10^{-4.4}$	-	-	8.1	A_m, K_L $K_F, 1/N$	242, 4.8, 82.5, 0.15	
						$CaCl_2$	0.05	8.1	A_m, K_L $K_F, 1/N$	119, 5.0 25.8, 0.24	
	14.3	4.2	30.0	-	$10^{-6} - 10^{-4.4}$	-	-	7.7	A_m, K_L $K_F, 1/N$	158, 4.5, 54.6, 0.15	
						$CaCl_2$	0.05	7.7	A_m, K_L $K_F, 1/N$	79.5, 4.7, 18.8, 0.22	
	10.7	2.0	16.5	-	$10^{-6} - 10^{-4.4}$	-	-	8.6	A_m, K_L $K_F, 1/N$	84, 4.8, 31.0, 0.14	
						$CaCl_2$	0.05	8.6	A_m, K_L $K_F, 1/N$	27, 5.1, 8.9, 0.18	
	5.4	1.0	8.7	-	$10^{-6} - 10^{-4.4}$	-	-	5.7	A_m, K_L $K_F, 1/N$	22, 4.4, 9.9, 0.11	
						$CaCl_2$	0.05	5.7	A_m, K_L $K_F, 1/N$	7.5, 4.4, 0.70, 0.37	

Table 14-1 (Contd). ADSORPTION CONSTANTS FOR LEAD

Adsorbent				Adsorbate		Electrolyte			Adsorption Measurements		Reference
Identity (a)		CEC meq/100g	S ₂ A ₂ m ² /g	Conc., M		Identity	Conc., M	pH	Constants (b)	Value (c)	
Soil	% Clay	% O.M.									
	12.0	3.1	16.2	-	10 ⁻⁶ - 10 ^{-4.4}	-	-	8.1	A _m , K _L , K _F , 1/N	108, 4.8, 56.3, 0.09	Soldatini et al. 1976 Riffaldi et al. 1976
						CaCl ₂	0.05	8.1	A _m , K _L , K _F , 1/N	57.5, 4.5, 7.9, 0.29	
	3.8	1.2	14.0	-	10 ⁻⁶ - 10 ^{-4.4}	-	-	5.8	A _m , K _L , K _F , 1/N	50, 4.3, 11.8, 0.20	
						CaCl ₂	0.05	5.8	A _m , K _L , K _F , 1/N	21, 4.3, 1.7, 0.38	
	7.0	1.8	23.7	-	10 ⁻⁶ - 10 ^{-4.4}	-	-	7.6	A _m , K _L , K _F , 1/N	170, 4.4, 77.8, 0.11	
						CaCl ₂	0.05	7.6	A _m , K _L , K _F , 1/N	56, 4.6, 7.0, 0.31	
	1.7	1.4	8.7	-	10 ⁻⁶ - 10 ^{-4.4}	-	-	8.1	A _m , K _L , K _F , 1/N	94, 4.1, 33.0, 0.13	
						CaCl ₂	0.05	8.1	A _m , K _L , K _F , 1/N	31, 4.8, 8.7, 0.23	
Sandy loam	-	59	-	10 ^{-3.9} - 10 ^{-3.0}		AlCl ₃	10 ^{-2.9} - 10 ^{-1.7}	3.1- 3.8	A _m , K _L	(3.1-5.6, 3.5-3.8)	Lagerwerff and Brower 1973
						CaCl ₂	10 ^{-2.5} - 10 ^{-1.6}	4.9- 6.3	A _m , K _L	(6.7-7.0, 4.8-5.6)	

Table 14-1 (Contd). ADSORPTION CONSTANTS FOR LEAD

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		Reference
Identity (a)	CEC meq/100g	S ₂ A ₂ m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
<u>Soil</u>									
Slit loam	205	-	10 ^{-3.9} - 10 ^{-3.0}	AlCl ₃	10 ^{-2.7} - 10 ^{-1.7}	3.1- 3.8	A _m , K _L	(4.3-10.7, 3.6)	Lagerwerff and Brower 1973
				CaCl ₂	10 ^{-2.5} - 10 ^{-1.6}	4.9- 6.3	A _m , K _L	(15.3-18.9, 5.3-6.0)	
Clay loam	184	-		AlCl ₃	10 ^{-2.5} - 10 ^{-1.7}	3.1- 3.8	A _m , K _L	(4.8-12.2, 3.4-4.1)	
				CaCl ₂	10 ^{-2.5} - 10 ^{-1.6}	4.9- 6.3	A _m , K _L	(17.9-19.6, 5.4-6.5)	
Sandy loam	59	-	10 ^{-3.9} - 10 ^{-3.0}	See above			K _{Al} ^{Pb} , K _{Ca} ^{Pb}	0.31, 4.13	Lagerwerff and Brower 1973
Slit loam	205	-	10 ^{-3.9} - 10 ^{-3.0}	See above			K _{Al} ^{Pb} , K _{Ca} ^{Pb}	0.11, 4.97	
Clay loam	184	-	10 ^{-3.9} - 10 ^{-3.0}	See above			K _{Al} ^{Pb} , K _{Ca} ^{Pb}	0.24, 11.1	
<u>Sediment</u>									
	29.7	-	10 ⁻⁷ - 10 ⁻⁶	-	-		7.4 K _F , 1/N	(0.42, 1.07)	Salim and Cooksey 1980
	1 hr							(1.08, 1.08)	
	3 hr							(2.21, 1.08)	
	7 hr							(5.99, 1.07)	
	15 hr							(6.15, 1.08)	
	∞								
	35.7	-	10 ^{-5.9} - 10 ^{-4.0}	-	-		- A _m , K _L	149, 5.4	Ramamoorthy and Rust 1978

Table 14-1 (Contd). ADSORPTION CONSTANTS FOR LEAD

Adsorbent				Adsorbate		Electrolyte		Adsorption Measurements		Reference
Identity (a)	CEC meq/100g	S ₂ A. m ² /g		Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
<u>Sediment</u>										
	% Clay	% O.C.						<u>Sediment</u>		
	12.6	3.34	-	-	10 ^{-4.3} - 10 ^{-3.3}	-	-	7.0	A _m , K _L	(21, 5.7)
	13.2	3.7	-	-	10 ^{-4.3} - 10 ^{-3.3}	-	-	7.4	A _m , K _L	(20, 4.9)
	3.6	0.81	-	-	10 ^{-4.3} - 10 ^{-3.3}			6.8	A _m , K _L	(20, 4.7)
	4.9	1.06	-	-	10 ^{-4.3} - 10 ^{-3.3}			7.1	A _m , K _L	(17, 4.9)

(a) O.C. = organic carbon

O.M. = organic matter

(b) K_{Ca}^{Pb}, K_{Al}^{Pb} = selectivity coefficientsA_m = Langmuir adsorption maximum, $\mu\text{mol g}^{-1}$ K_L = Langmuir Constant, $\log \text{M}^{-1}$ A_m^I, K_L^I, A_m^{II}, K_L^{II} = two adsorption sites*K₁^S, *K₂^S = surface complexation constants for ionic species, logK^{Int} = Intrinsic adsorption constant for ionic species, logK_C^I = affinity constant, logK_F, 1/N = Freundlich constants for A = K_FC^{1/N}; A = $\mu\text{mol g}^{-1}$; C = μM

(c) () = estimated values

Section 15

MANGANESE

Manganese (Mn) is a multivalent element that forms several solids in its +2, +3, and +4 oxidation states with +3 and +4 solids being more stable in oxidizing conditions and +2 solids more stable under reducing conditions. Manganese(II) is the primary oxidation state in aqueous solutions. Very limited information is available on precipitation/dissolution and adsorption/desorption mechanisms. The available data suggests that MnCO_3 may be the solubility-controlling solid under reducing conditions and high pH and CO_2 levels. Limited studies indicate that at low Mn concentrations ($<10^{-4}$ M), specific adsorption is the dominant retention mechanism while ion exchange is the dominant retention mechanism at higher Mn concentrations.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIES

Manganese is a multivalent element and can exist in +2, +3, +4, and +7 oxidation states. Manganese +2, +3, and +4 oxidation states form environmentally important solid phases. Manganese(II) is the most stable and dominant aqueous oxidation state, although Mn(III) and Mn(VII) also occur in solution. Lindsay (1979) has recently reviewed the thermodynamic data of Mn compounds and has calculated the relative stability of Mn compounds. His calculations show that Mn(IV) and Mn(III) compounds can occur under oxidizing conditions while Mn(II) compounds can occur under reducing conditions. Pyrolusite ($\beta\text{-MnO}_2$) appears to be the most stable compound under oxidizing conditions ($\text{pe} + \text{pH} > 16.6$). Because small quantities of foreign ions interfere with the formation of $\beta\text{-MnO}_2$ (McKenzie 1977), pyrolusite is unlikely to form in soils. Manganese(III) and Mn(IV) containing nsutite ($\gamma\text{-MnO}_{1.9}$) are the second most stable species and readily form in soils (Zwicker et al. 1962; Jones and Milne 1956), only under oxidizing conditions. Other Mn oxides (MnOOH , Mn_2O_3 , Mn_3O_4) are expected to form under low CO_2 and moderately reducing conditions. Under reducing conditions and in the presence of CO_2 , rhodochrosite (MnCO_3) is expected to form in soils.

To determine the relative abundance of Mn(II) species in ground waters representative of utility waste leachates, the activities of different Mn(II) when Mn^{2+}

fixed at 10^{-5} M or controlled by MnCO_3 were plotted (Figure 15-1) using the thermodynamic data reported by Ball et al. (1980). Below pH values of about 9.3, Mn^{2+} followed by MnSO_4^0 are the dominant species. At higher pH values (>10) MnHCO_3^+ and MnOH^+ become the important aqueous species. All of the other Mn(II) complexes [such as MnCl^+ , MnF^+ , $\text{Mn}(\text{NO}_3)_2^0$] do not contribute significantly to the total soluble Mn.

PRECIPITATION/DISSOLUTION

Precipitation/dissolution studies examining Mn aqueous concentrations are limited. The data presented in Figure 15-1 showed that the MnCO_3 maintains low Mn activities and may be the solubility-controlling solid under reducing and relatively high pH and CO_2 levels. Ponnampetuma et al. (1969) suggest the presence of MnCO_3 at low redox and other Mn oxides at higher redox values. Pasricha and Ponnampetuma (1976) showed that MnCO_3 may be the solubility-controlling solid for Mn^{2+} levels observed in soils. Based on Mn^{2+} levels in soils maintained at constant redox and CO_2 pressures, Schwab and Lindsay (1983) showed that Mn^{2+} levels at low redox potentials ($\text{pe} + \text{pH} < 15$) appear to be controlled by MnCO_3 while at high redox potentials by Mn

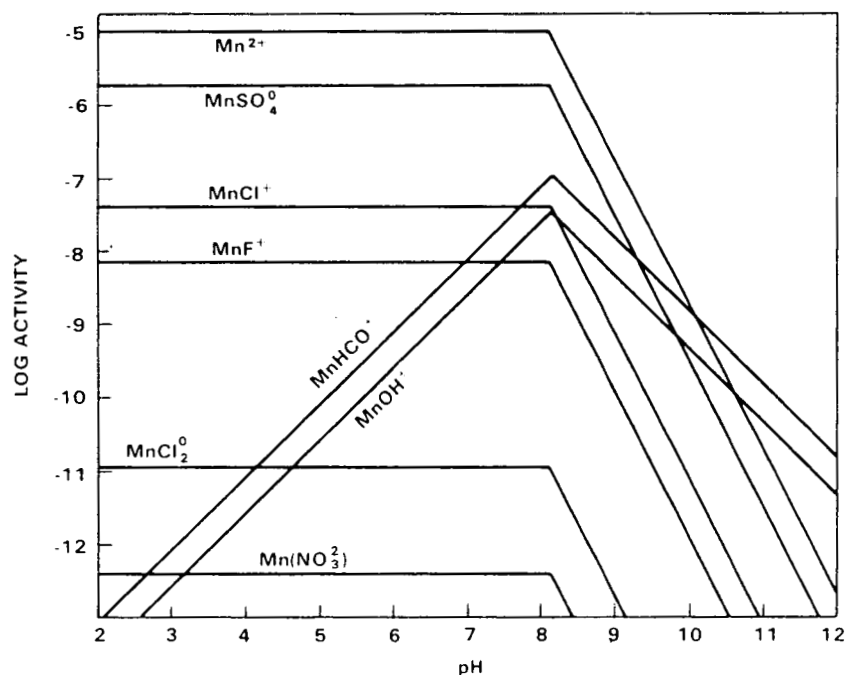


Figure 15-1. Activities of different Mn(II) species when activity of Mn^{2+} is fixed at 10^{-5} or controlled by rhodochrosite (MnCO_3), $\text{SO}_4^{2-} = \text{Cl}^- = 10^{-3}$, $\text{F}^- = \text{NO}_3^- = 10^{-4}$ and $\text{CO}_2(\text{gas}) = 10^{-3.52}$ atmospheres.

oxides. Schwab and Lindsay (1983) also compared the activities of Mn^{2+} from the data reported by several authors (Pasricha and Ponnampersuma 1976; Ponnampersuma et al. 1969; Stollenwerk and Runnels 1979) to the $MnCO_3$ solubility and showed that $MnCO_3$ may have been the solubility-controlling solid. McBride (1979a) observed chemisorption of Mn by $CaCO_3$ which he suggests may possibly lead to the formation of $MnCO_3$.

ADSORPTION/DESORPTION

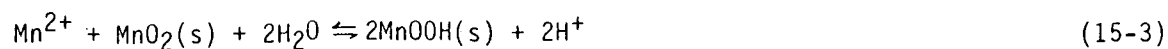
Manganese is an essential micronutrient, yet, its adsorption by soil has been neglected in the agronomic literature. Manganese adsorption is complicated by redox reactions that affect aqueous species and transformations and formation of Mn compounds of different oxidation states.

The available literature does not allow a clear definition of the adsorption process (Table 15-1) most important in Mn retention by soil (e.g., specific adsorption, ion exchange or organic complexation). Regression analysis of the dependency of Mn(II) adsorption capacity on soil properties commonly points to the importance of cation exchange capacity (Curtin et al. 1980, Shuman 1977a), thus suggesting an ion exchange retention mechanism at higher solution concentrations of Mn ($>10^{-4}$ M). However, the adsorption capacity of many soils for Mn is usually far less than the cation exchange capacity (Shuman 1977). Complexation by soil organic matter may occur, strongly influencing adsorption at lower Mn(II) concentrations (Hemstock and Low 1953). Clay minerals and hydrous iron oxide adsorb Mn less strongly than Co, Ni, Zn, and Cu (Takematsu 1979). Manganese is weakly, but specifically adsorbed by iron oxide (Takematsu 1979); and more strongly by various Mn oxides (Takematsu 1979, Murray 1975). In calcareous materials, chemisorption to $CaCO_3$ surfaces occurs, possibly leading to formation of $MnCO_3$ (McBride 1979).

The adsorption of Mn by clay minerals (Reddy and Perkins 1976; Hemstock and Low 1973), Fe oxides (McKenzie 1980), and Mn oxides (McKenzie 1980; Murray 1975; McKenzie 1979) usually results in the release of 1.5 to 1.6 moles of H^+ for each mole of Mn adsorbed at total $Mn^{2+} < 10^{-6}$ M. For most surfaces, complexation by hydroxylated Fe, Mn, or Al accounts for the release of H^+ :



However, the oxidation of the manganous ion at the surface of Mn oxides and incorporation into a new surface solid phase may account for its removal from solution (McKenzie 1980; Posselt et al. 1978).



The adsorption of transition metals by soil (Doner et al. 1982) or Mn oxides (Murray 1975) may release Mn(II) from the solid. This results from ion exchange of adsorbed Mn by a more strongly binding metal (Doner et al. 1982) or from structural replacement of Mn in the Mn oxide (Doner et al. 1982; Loganathan et al. 1977).

Table 15-1. ADSORPTION CONSTANTS FOR MANGANESE

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		Reference
Identity (a)	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
Clay Minerals									
Bentonite	-	-	0 - 10 ^{-3.0}	-	-	4.9	A _m , K _L , K _F , 1/N	(126, 1.9, 0.011, 0.94)	Reddy and Perkins 1976
						6.2	A _m , K _L , K _F , 1/N	(83, 3.0, 7.8, 0.26)	
						7.6	A _m , K _L , K _F , 1/N	(130, 3.2, 23, 0.18)	
Illite	-	-	0 - 10 ^{-3.0}	-	-	8.8	A _m , K _L , K _F , 1/N	(186, 3.3, 4.3 0.48)	
Kaolinite	-	-	0 - 10 ^{-2.9}			4.9	K _F , 1/N	(0.015, 1.13)	
						6.2	"	(0.011, 1.20)	
						7.6	"	(0.018, 1.17)	
						8.8	"	(0.043, 1.07)	
Montmorillonite	70	-	0.005 - 0.05	-	-	5-6	A _m , K _L	(370, 2.8)	Stuanes 1976
	96	-	0.005 - 0.05					(610, 2.7)	
Kaolinite	4	-	0.005 - 0.05	-	-	5-6	A _m , K _L	(18, 2.9)	
Vermiculite	70	-	0.005 - 0.05	-	-	5-6	A _m , K _L	(480, 2.7)	
Feldspar-Albite	>0.6	-	0.005 - 0.05	-	-	5-6	A _m , K _L	(1.3, 2.8)	
Labradorite	<2.5	-	0.005 - 0.05	-	-	5-6	A _m , K _L	(9.1, 3.5)	

Table 15-1 (Contd). ADSORPTION CONSTANTS FOR MANGANESE

Adsorbent			Absorbate		Electrolyte			Adsorption Measurements		Reference	
Identity (a)	CEC meq/100g	S _A m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)			
<u>Mn Oxides</u>											
Birnessite (δ -MnO ₂)	-	98	10 ⁻³ - 10 ^{-2.2}	KNO ₃	0.1	5	A _m , K _L	(1590, 3.6)	McKenzie 1980		
Cryptomelane (α -MnO ₂ as K ₂ Mn ₈ O ₁₆)	-	206	10 ⁻³ - 10 ^{-2.2}	KNO ₃	0.1	5	A _m , K _L	(1130, 3.5)			
Hydrous MnO ₂ sol- coprecipitation	-	-	0 - 10 ^{-2.7}	NaClO ₄	0.01	5	A _m , K _L	(3230, 1.6)	Posselt et al. 1968		
γ -MnOOH	-	56	10 ⁻⁸ - 10 ⁻⁶	Seawater	~0.7	8	K _d	30	Takematsu 1979		
γ MnO ₂	-	33	10 ⁻⁸ - 10 ⁻⁶	"	~0.7	8	K _d	3000			
δ -MnO ₂	-	61	10 ⁻⁸ - 10 ⁻⁶	"	~0.7	8	K _d	50,000			
<u>Fe Oxides</u>											
Hydrated Fe Oxide	-	215	10 ^{-7.8} - 10 ^{-5.8}	Seawater	~0.7	8	K _d	20	Takematsu 1979		
<u>Calcite</u>											
Fine	~1.1	0.49	10 ⁻³ - 10 ⁻⁶	-	-	~8	A _m , K _L	(9.8, 4.3)	McBride 1979		
Coarse	~0.5	0.22	10 ⁻³ - 10 ⁻⁶	-	-	~8	A _m , K _L	(8.7, 5.2)			
<u>Soil</u>											
	$\%$ Clay	$\%$ O.M.									
Clay loam A	28.1	2.37	12.43	-	0 - 10 ^{-2.9}	Na ₂ SO ₄	0.01	5.4	A _m , K _L	14.7, 3.4	Shuman 1977
B2t	48.3	0.10	9.85	-	0 - 10 ^{-2.9}	Na ₂ SO ₄	0.01	5.7	A _m , K _L	19.3, 3.4	
Sand loam A	7.6	1.60	4.94	-	0 - 10 ^{-2.9}	Na ₂ SO ₄	0.01	6.7	A _m , K _L	8.7, 4.0	
B2t	36.0	0.07	5.98	-	0 - 10 ^{-2.9}	Na ₂ SO ₄	0.01	5.2	A _m , K _L	8.0, 3.5	

Table 15-1 (Contd). ADSORPTION CONSTANTS FOR MANGANESE

Adsorbent			Adsorbate		Electrolyte		Adsorption Measurements		Reference		
Identity (a)			CEC	S ₂ A.							
Identity			meq/100g	m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
Soil											
Clay			O.M.								
Loam sand A	5.1	0.92	3.20	-	0-10 ^{-2.9}	Na ₂ SO ₄	0.01	5.4	A _m , K _L	0.91, 4.2	Shuman 1977
B2t	40.4	0.12	5.32	-	0-10 ^{-2.9}	Na ₂ SO ₄	0.01	5.8	A _m , K _L	9.3, 3.6	
Loam sand A	2.4	1.14	3.13	-	0-10 ^{-2.9}	Na ₂ SO ₄	0.01	5.3	A _m , K _L	0.91 4.3	
B2t	14.7	0.03	2.62	-	0-10 ^{-2.9}	Na ₂ SO ₄	0.01	5.4	A _m , K _L	3.3, 3.7	
Soil											
	22.4	1.51	19.5	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	8.2	A _m	49	Curtin et al. 1980
	66.4	0.86	41.9	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	8.0	"	74	
	55.4	0.58	42.2	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	8.0	"	77	
	64.4	0.10	15.1	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	8.1	"	48	
	21.4	0.43	11.3	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	8.1	"	38	
	75.4	1.30	47.8	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	8.2	"	70	
	51.4	0.54	36.9	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	8.2	"	69	
	44.4	0.95	29.1	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	8.0	"	61	
	48.4	0.40	16.7	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	7.1	"	42	
	74.4	0.56	36.4	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	7.7	"	68	
	51.4	0.46	37.4	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	8.0	"	64	
	69.4	0.50	42.7	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	7.9	"	72	
	62.4	0.52	33.4	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	8.0	"	63	
	26.4	1.43	9.1	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	6.9	"	31	
	55.4	0.34	14.8	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	7.0	"	41	
	28.4	0.54	15.4	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	8.2	"	50	
	63.0	0.95	56.6	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	8.0	"	79	
	41.0	0.59	41.9	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	8.0	"	69	
	17.0	0.19	45.0	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	7.5	"	68	
	45.0	0.84	33.4	-	10 ^{-3.7} - 10 ^{-2.6}	-	-	7.0	"	60	
Sediment											
Indigenous Mn and Ca			46.5-68.3	-	-	Seawater	~0.7	~8	Mn K _{Ca}	0.23-2.7	Menon 1980

(a) O.M. = organic matter

(b) A_m = Langmuir adsorption maximum, $\mu\text{mol g}^{-1}$ K_L = Langmuir constant, $\log \text{M}^{-1}$ K_F, 1/N = Freundlich constants for $A = K_F C^{1/N}$; A = $\mu\text{mol g}^{-1}$; C = μM K_d = distribution coefficient, g g^{-1} K_{Ca}^{Mn} = selectivity coefficient

(c) () = estimated values

Section 16

MERCURY

Mercury (Hg) in aqueous solutions can exist in several different oxidation states (0, +1, +2) depending on the redox potential. Hg(II) forms strong complexes with many ligands including halides. Under oxidizing conditions where Hg(II) compounds are fairly soluble, the primary attenuation mechanism of Hg is expected to be adsorption/desorption. Particulate organic carbon and hydrous oxides of Fe and Mn appear to be the most important adsorbents when Hg is present in low concentrations ($<10^{-5}$ M). Complexing ligands (such as halides) decrease adsorption but the effect of competing ions has not been defined.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIATION

Mercury is a multivalent element and in aqueous solutions can exist in 0, +1, and +2 oxidation states. Lindsay (1979) has recently reviewed the chemistry of Hg in soils. Using the thermodynamic data reported by Lindsay (1979), information regarding stabilities of solid and aqueous species were developed. The relative solubilities of Hg solids as a function of pH and at various redox levels is presented in Figures 16-1, 16-2, and 16-3. All solid phases reported in Table A-6 were considered while constructing Figures 16-1 through 16-3. However, the solubility of the solid phases changes dramatically with changes in redox potential; solids not shown in any given figure are too soluble to fall within the graph boundaries. Figure 16-1 shows the solubility of Hg solids in terms of Hg^{2+} versus pH under oxidizing conditions (pe + pH 16). Mercuric iodide (HgI_2) is the least soluble solid at pH < 8, with $\text{Hg}_2\text{I}_2(\text{c})$ and $\text{HgCO}_3(\text{c})$ becoming nearly as insoluble as $\text{HgI}_2(\text{c})$ at high pH. The formation constant for $\text{HgCO}_3(\text{c})$ is of unknown quality and should be viewed as only an estimate.

The concentrations of Hg^0 supported by different Hg solids is plotted as a function of pH at pe + pH 9 in Figure 16-2. Liquid mercury [$\text{Hg}(\text{l})$] is predicted to be the least soluble phase above pH 3.8. The solubilities of the iodides of Hg depend upon I^- concentrations, and I^- levels will dictate the conditions under which $\text{Hg}_2\text{I}_2(\text{c})$ will control Hg^0 levels. The relative solubility of Hg solids under reduced conditions (pe + pH 4) is given in Figure 16-3. Under these conditions, $\alpha\text{-HgS}$ is the least soluble compound.

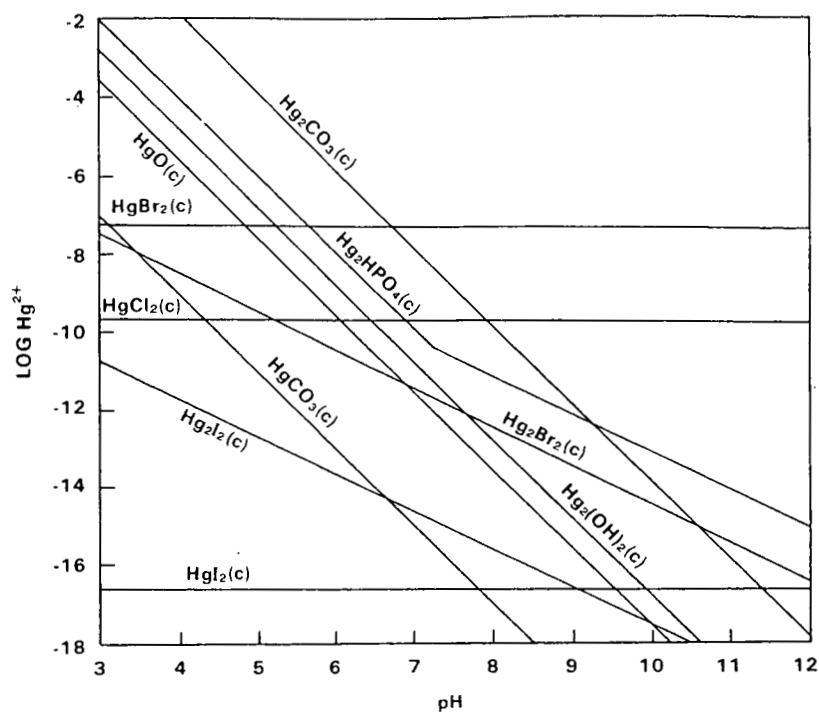


Figure 16-1. Relative solubility of Hg solid phases under oxidizing conditions ($pe + pH = 16$) when activities of $Cl^- = SO_4^{2-} = 10^{-3}$, $I^- = Br^- = 10^{-6}$, $\Sigma P = 10^{-6}$, and $CO_2(gas) = 10^{-3.52}$ atmospheres.

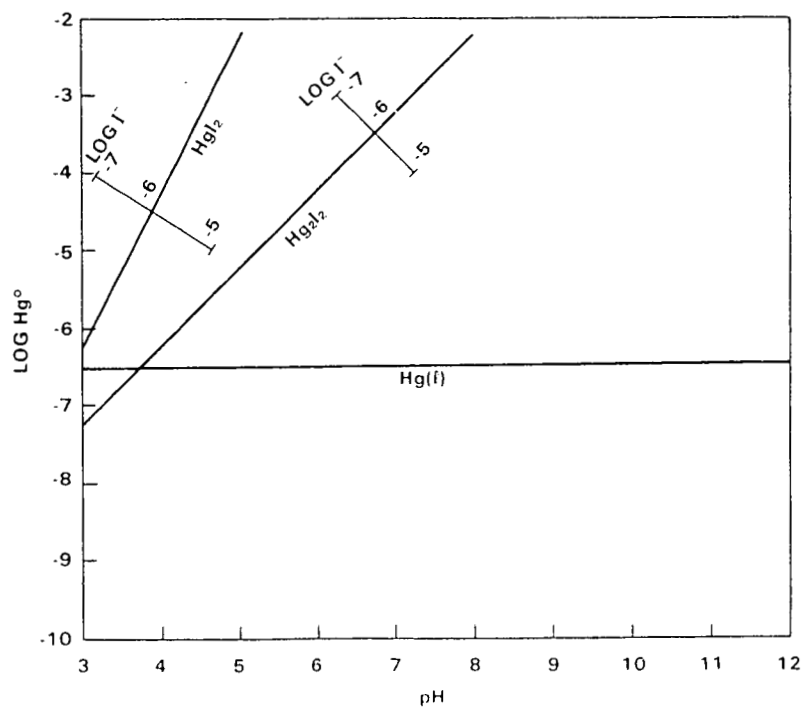


Figure 16-2. Relative solubility of Hg solids at $pe + pH = 9.0$.

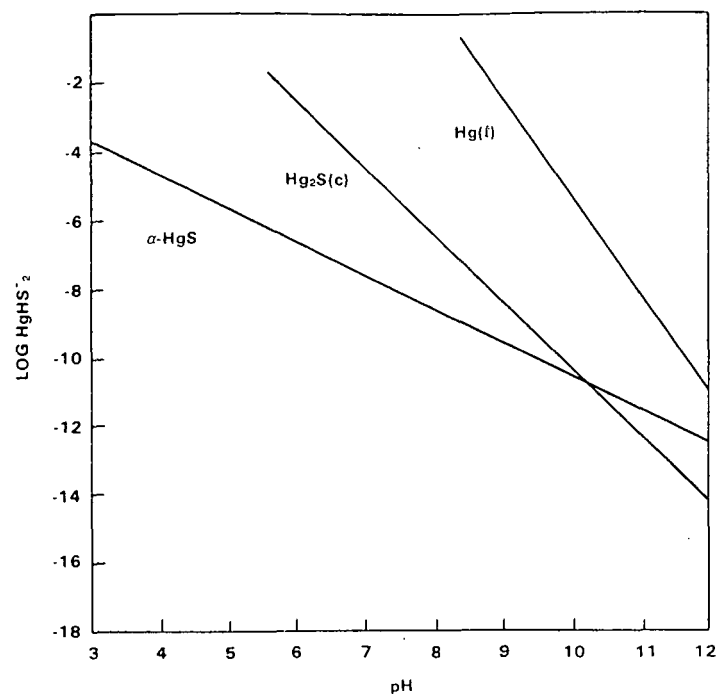


Figure 16-3. The relative solubility of Hg solids under reducing conditions ($pe + pH = 4$) when $\Sigma S = 10^{-6}$ M.

Figures 16-1 through 16-3 are useful in determining relative stability or solubility of compounds, but are not useful in predicting the nature of dominant aqueous species and the total concentrations of Hg expected to be in equilibrium with the solids under different environmental conditions. Therefore, Figures 16-4 through 16-6 were constructed. In Figure 16-4, concentrations of various complexes in equilibrium with $HgI_2(c)$ at $pe + pH = 16$ are plotted versus pH. Complexes containing I^- are by far the most important over the pH range 3 to 9. $Hg(OH)_2^0(aq)$ becomes dominant at pH values >9 . The concentration of HgI_2^0 , the predominant species, would be $10^{-4.53}$ (6 mgL^{-1}) at all pH values and all I^- concentrations as long as $HgI_2(c)$ persists. Among the compounds considered above, $HgI_2(c)$ is the most stable under oxidizing conditions (Figure 16-1). Because even $HgI_2(c)$ is very soluble (Figure 16-4), it is unlikely that any of the solids discussed would form in oxidized environments.

In Figure 16-5, equilibrium is assumed with $Hg(l)$ at $pe + pH = 9$. Hg^0 would predominate above pH 4 with a concentration of $10^{-6.52}$ M. The solubility of Hg in

ADSORPTION/DESORPTION

Considerable evidence suggests that organic material is the most important factor controlling Hg adsorption in soils (Hogg et al. 1978, John et al. 1975) and on sediments (Ramamoorthy and Rust 1978, Rogers et al. 1981, Ramamoorthy and Rust 1976, Miller 1975). Regardless of pH, the affinity of humic acid (Kerndorf and Schnitzer 1980) or organic-rich sediments (Ramamoorthy and Rust 1978) for Hg is stronger than most other trace metals (Cd, Cu, Zn). The hydrous oxides may also be important adsorbents of Hg in soil. Manganese oxide is of particular importance and has high affinity and adsorption capacity for Hg (Lockwood and Chen 1973). The adsorption rate of Hg on sediment is 10^3 to 10^5 times greater than the rate of desorption (Rogers et al. 1981). However, with time, microbial processes may lead to the formation of elemental Hg, which is released to water even in the presence of humic acid (Miller 1975). Although methyl-Hg is also adsorbed (Reimers and Krenkel 1974) or may be synthesized in soils treated with inorganic Hg (Hogg et al. 1978), it does not appear to accumulate due to its volatility or subsequent degradation.

Mercury adsorption is influenced by pH (Table 16-1). On some model adsorbents such as silica (MacNaughton and James 1974) and Fe oxides (Inoue and Munemori 1979, Forbes et al. 1974), Hg exhibits a distinct adsorption edge. However, in the absence of Cl^- , the adsorption of inorganic Hg on many adsorbents is high and not strongly affected by changes in pH between 5 and 8. Though an explanation is not available, Hg adsorption on certain adsorbents may decrease at pH levels above 8 (Lockwood and Chen 1973, MacNaughton and James 1974) in contrast to other cationic metals. Experimental evidence indicates that the predominant inorganic aqueous species in this pH range, $\text{Hg}(\text{OH})_2^0$, is the adsorbing species (Kinniburgh and Jackson 1978; Lockwood and Chen 1973, 1974; Reimers and Krenkel 1974; Bruninx 1975; Forbes et al. 1974; Inoue and Munemori 1979). The coordinated hydroxyl groups appear to act as bridging ligands between the adsorbent surface and Hg (Forbes et al. 1974). A pronounced reduction in Hg adsorption occurs at lower pH in the presence of Cl^- (Kinniburgh and Jackson 1978; Lockwood and Chen 1973, 1974; MacNaughton and James 1974; Reimers and Krenkel 1974; Forbes et al. 1974; Inoue and Munemori 1979). This results from the formation of stable Hg-chloride complexes, primarily HgCl_2^0 , which are poorly adsorbed (Kinniburgh and Jackson 1978).

The formation of $\text{Hg}(\text{OH})_2^0$, a crucial step in the adsorption behavior of Hg, is strongly dependent on the concentration and type of halide ions in the adsorbate medium. Chloride, Br^- and perhaps I^- suppress Hg adsorption (Inoue and Munemori 1979) through formation of stable aqueous complexes. Fluoride has little effect on Hg adsorption.

The adsorption of Hg by several soil constituents in the presence of Cl^- (Table 16-1) has been studied in detail (Kinniburgh and Jackson 1978; Lockwood and Chen 1973, 1974; Newton et al. 1976; Frenet-Robin and Ottmann 1978; Reimers and Krenkel 1974; Bruninx 1975; Forbes et al. 1974; Inoue and Munemori 1978; Hahne and Kroontje 1973). The neutral Cl complex (HgCl_2^0) is not adsorbed by hydrous Fe oxide gel (Kinniburgh and Jackson 1978, Bruninx 1975) or goethite (Forbes et al. 1974), but may be weakly adsorbed by silica (MacNaughton and James 1974), hydrous Mn oxides (Lockwood and Chen 1974), illite and montmorillonite (Reimers and Krenkel 1974). The presence of Cl^- hinders Hg^{2+} adsorption to carboxyl groups, but has little effect on interaction with amine or thiol groups in artificial sediments (Reimers and Krenkel 1974). Mercury exhibited significant mobility in column studies using simulated solid waste leachate and eleven soils from seven prominent soil orders (Korte et al. 1976). The mobility in all soils was greater than that observed for Cu, Pb, Be, Zn, and Ni and likely results from Cl^- complexation; HCl was added to the leachate to retard precipitation.

With the exception of the effect of the halides, Hg adsorption is relatively insensitive to electrolyte concentration (MacNaughton and James 1974; Newton et al. 1976). However, the rate of adsorption is reduced by increased NaClO_4 concentration (MacNaughton and James 1974). A small percentage (<0.3%) of Hg applied to soil in sewage effluent is removed by selective chemical extractants (CaCl_2 , NH_4OAc , EDTA or DTPA) (Hogg et al. 1978), suggesting the poor desorbability of soil-adsorbed Hg. Increasing acid hydrolysis using strong mineral acid (6N HCl), however, produces greater release of Hg (up to 90%). In contrast, >70% of Hg applied as $\text{Hg}(\text{NO}_3)_2$ is desorbed from sediments by NaCl or nitrilotriacetate (NTA) (Ramamoorthy and Rust 1978). The extractability or desorbability of Hg depends on its distribution between organic and inorganic adsorbents. Mercury may bond strongly with certain functional groups on soil organic matter; hence, Hg is less readily removed from organic-rich substrates.

Table 16-1. ADSORPTION CONSTANTS FOR MERCURY

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		References
Identity ^(a)	CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants ^(b)	Value ^(c)	
Fe ₂ O ₃ ·H ₂ O(am)	-	-	2.5 × 10 ⁻⁵ M	NaNO ₃	1.0	4.5	K _d	2.08	Kinniburgh and Jackson 1978
				NaNO ₃ + NaCl	1.0, 10 ⁻⁴	4.5	K _d	0.41	
				NaNO ₃ + CaCl ₂	1.0, 10 ^{-4.3}	4.5	K _d	0.449	
				NaNO ₃	1.0	5.95	K _d	82.8	
				NaNO ₃ + NaCl	1.0, 10 ⁻⁴	5.95	K _d	46.2	
				NaNO ₃ + CaCl ₂	1.0, 10 ^{-4.3}	5.95	K _d	43.7	
MnO ₂ (am)			10 ⁻⁷ - 10 ⁻⁶	-	-	6-8	K _F , 1/N	9120	Lockwood and Chen 1973
Fe(OH) ₃ (am)	-	-	10 ⁻⁷ - 10 ⁻⁶	-	-	5-8	K _F , 1/N	90.8, 0.76	Lockwood and Chen 1974
SiO ₂	-	5.0	10 ⁻⁷	H ₂ SiO ₄	0.1	1-11			MacNaughton and James 1974
				H ₂ SiO ₄ +NaCl	0.1		K _E	-3.2	
				NaCl	0.0				

Table 16-1 (Contd). ADSORPTION CONSTANTS FOR MERCURY

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		References	
Identity (a)	CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)		
Bentonite	-	-	10 ⁻⁶	Ca(NO ₃) ₂	0.01	6.7	K _d	408	Newton et al. 1976	
						7.9	K _d	179		
						8.9	K _d	119		
						10.2	K _d	141		
						11.0	K _d	163		
				CaCl ₂	0.01	pH				
							6.6	K _d	30.0	
							8.1	K _d	58.5	
							8.9	K _d	141.	
							10.5	K _d	164	
							10.9	K _d	224	
Soil										
Asquith clay-8.8%, Org C.-0.79%	7.23		10 ⁻⁶ - 10 ⁻⁴	CaCl ₂	0.01	6.6	A _m	1.6	Hogg et al. 1978	
Oxbow clay-45.5%, Org C.-2.98%	26.0					7.6	A _m	12.3		
Sediments									Ramamoorthy and Rust 1978	
	O.C., %	Particle size, mm								
0.6	0.44	-	-	10 ⁻⁶ - 10 ⁻⁴	-	-	-	A _m , K _L		11.9, 5.9
3.2	0.007	-	-	10 ⁻⁶ - 10 ⁻⁴	-	-	-	A _m , K _L		55.8, 6.26
5.2	0.12	-	-	10 ⁻⁶ - 10 ⁻⁴	-	-	-	A _m , K _L		118, 5.91
35.7	0.16	-	-	10 ⁻⁶ - 10 ⁻⁴	-	-	-	A _m , K _L		53.6, 6.5
0.6	0.40	-	-	10 ⁻⁶ - 10 ⁻⁴	-	-	-	A _m , K _L	13.0, 5.73	

Table 16-1 (Contd). ADSORPTION CONSTANTS FOR MERCURY

Adsorbent				Adsorbate		Electrolyte			Adsorption Measurements		References	
Identity (a)		CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)			
Sediments		Particle										
O.C., %		size, mm										
2.4		0.27	-	-	10 ⁻⁶ - 10 ⁻⁴	-	-	-	A _m , K _L	16.7, 5.5		
1.3		0.01	-	-	10 ⁻⁶ - 10 ⁻⁴	-	-	-	A _m , K _L	237, 5.9		
1.2		0.23	-	-	10 ⁻⁶ - 10 ⁻⁴	-	-	-	A _m , K _L	41.9, 6.33		
94.5		0.25	-	-	10 ⁻⁶ - 10 ⁻⁴	-	-	-	A _m , K _L	96.4, 6.02		
0.6		0.16	-	-	10 ⁻⁶ - 10 ⁻⁴	-	-	-	A _m , K _L	13.46, 6.11		

(a) O.C. = organic matter

(b) K_d = distribution coefficient, l g⁻¹ except Neuton et al. (1976) values in ml g⁻¹K_F, 1/N = Freundlich constants for A = K_FC^{1/N}; A₁ μmol g⁻¹; C, μMK_E = exchange coefficient, logA_m = Langmuir adsorption maximum, μmol g⁻¹K_L = Langmuir constant, log M⁻¹E_H = redox potential, mv

Section 17

MOLYBDENUM

Molybdenum (Mo) is a multivalent element, found primarily in +6 valence state in aqueous solutions. In relatively dilute solutions of Mo where polynuclear species are not important, MoO_4^{2-} is the dominant aqueous species at pH values >4.3 . Precipitation/dissolution and adsorption/desorption reactions of Mo have not been studied extensively. The available data suggest the possibility of iron molybdate as one of the important solubility-controlling solids. It appears PbMoO_4 may also be an important solubility-limiting solid. Adsorption primarily occurs at low pH values on hydrous oxides and amorphous aluminosilicates. Phosphate has been observed to be a strong competitor for Mo adsorption sites.

RELATIVE STABILITIES OF SOLID AND AQUEOUS SPECIES

Molybdenum can exist in +3, +4, +5, and +6 valence states. However, in aqueous solutions, only the +6 state has stability over a broad range of pH and Eh (Baes and Mesmer 1976). The solubilities of different Mo solids in terms of equilibrium MoO_4^{2-} activities are plotted as a function of pH (Figure 17-1). The solubilities of the metal molybdates [CoMoO_4 , ZnMoO_4 , $\text{Fe}_2(\text{MoO}_4)_3$, and PbMoO_4] depend on the aqueous activities of the metal ions. For instance, if FeOOH (goethite) were assumed to control Fe^{3+} activity rather than $\text{Fe}(\text{OH})_3(\text{am})$, the solubility of $\text{Fe}_2(\text{MoO}_4)_3$ would increase due to the decreased levels of Fe^{3+} . The relative solubilities of Mo compounds decrease in the following order: CoMoO_4 , ZnMoO_4 , $\text{MoO}_3(\text{c})$, $\text{H}_2\text{MoO}_4(\text{c})$, $\text{Fe}_2(\text{MoO}_4)_3$, PbMoO_4 . The broken lines (Figure 17-1) in the PbMoO_4 plot serve as a reminder that Pb is of limited abundance in most environments. If Pb^{2+} activity is assumed to be 10^{-5} M , then the minimum solubility of PbMoO_4 in terms of MoO_4^{2-} would be approximately 10^{-8} M . This type of information is useful when measuring or predicting the solubility of trace elements in soils and sediments.

The distribution of the $\text{H}_n\text{MoO}_4^{n-2}$ and polynuclear species of Mo in equilibrium with $\text{Fe}_2(\text{MoO}_4)_3$ and $\text{Fe}(\text{OH})_3(\text{am})$ is plotted as a function of pH in Figure 17-2. MoO_4^{2-} is the dominant species above pH 4.3. H_2MoO_4^0 dominates below pH 4. Cationic and polynuclear Mo species are unimportant in this system. However, the polynuclear species will become important if the concentrations of MoO_4^{2-} are high enough.

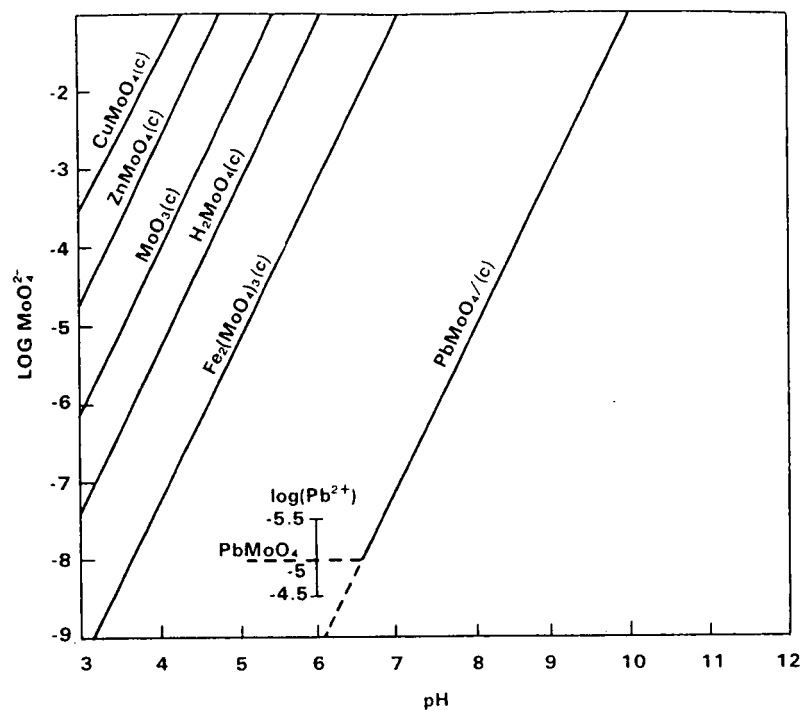


Figure 17-1. Relative solubilities of Mo solid phases when the activities of Cu, Zn, Fe, Pb are controlled by CuFe_2O_4 , soil Zn (Lindsay 1979), $\text{Fe}(\text{OH})_3(\text{am})$, and PbCO_3 [$\text{CO}_2(\text{gas}) = 10^{-3.52}$] or $\text{Pb}^{2+} = 10^{-5} \text{ M}$, respectively.

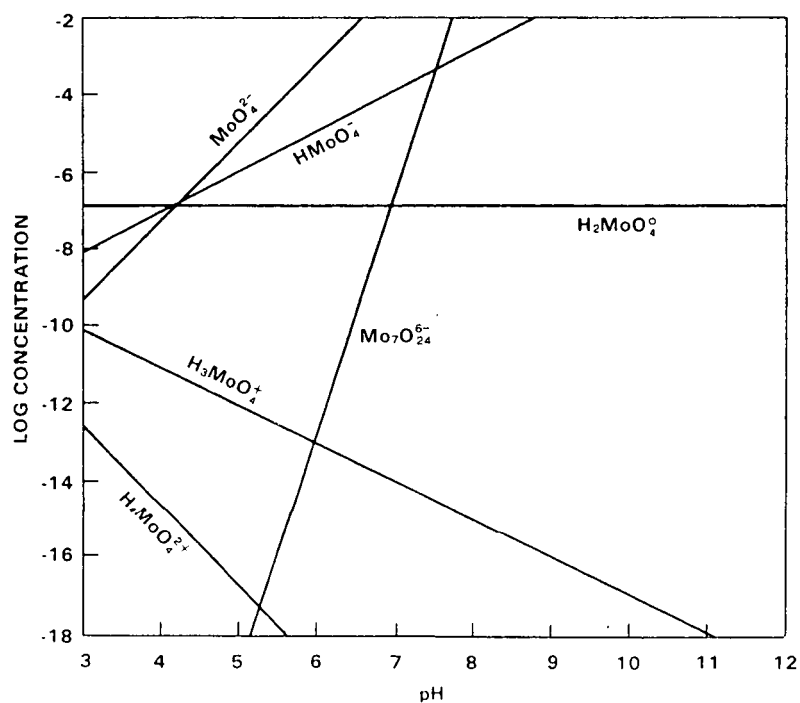


Figure 17-2. The activities of Mo aqueous species in equilibrium with $\text{Fe}_2(\text{MoO}_4)_3$ when Fe activities are controlled by $\text{Fe}(\text{OH})_3(\text{am})$.

PRECIPITATION/DISSOLUTION

Solubility-controlling solids in soils and subsoils have not been definitely identified, though their presence has been suggested by several studies. Barrow (1974a) found that desorption of previously adsorbed MoO_4^{2-} became increasingly difficult with time. This conversion to a form which is difficult to desorb is consistent with the formation of an insoluble solid phase. Hem (1977) suggested that Mo solubility in natural environments may be controlled by ferrous molybdate. Reisenauer et al. (1962) showed that proton consumption and water loss during sorption of MoO_4^{2-} on ferric oxide was consistent with the formation of $\text{Fe}_2(\text{MoO}_4)_3$, ferric molybdate. Reyes and Jurinak (1967) also hypothesized the formation of iron molybdate in Mo adsorption experiments with hematite.

Vlek and Lindsay (1977) measured the solubility of Mo in soils ranging from pH 5.5 to 7.7. They found that the solubility of Mo did not follow the trends expected from theoretical considerations. Vlek and Lindsay (1977) used thermodynamics to demonstrate that PbMoO_4 (wulfenite) should be the most stable Mo compound in soil, but when PbMoO_4 was added to the soils, the MoO_4^{2-} concentrations increased. It was concluded that adsorption reactions may be responsible for controlling Mo in soils.

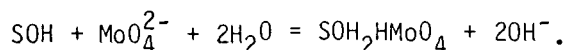
ADSORPTION/DESORPTION

The adsorption behavior of Mo in soils is strongly influenced by the presence of Fe and Al oxides over a wide range in MoO_4^{2-} concentrations (Barrow 1970; Karimian and Cox 1978). Amorphous aluminosilicates (e.g., allophane) also have high affinity for Mo (Gonzalez et al. 1974). Available evidence suggests that the principal adsorbing species of Mo is HMoO_4^- (Reyes and Jurinak 1967). Though a mechanism has not been established, soil organic matter has also been proposed as an important factor in controlling adsorption from aqueous solutions containing low concentrations of Mo (Bloomfield and Kelso 1973; Karimian and Cox 1978).

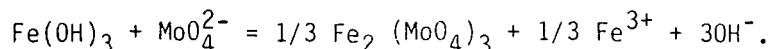
Solution pH and ionic strength may strongly influence Mo adsorption (Table 17-1). Less adsorption of MoO_4^{2-} occurs on soils and soil minerals as pH increases due to increasing negative charge density on amphoteric hydrous oxides or functional groups (Hingston et al. 1972; Karimian and Cox 1973; Pasricha and Randhawa 1977; Theng 1971). This phenomenon is comparable to that observed for other anions (e.g., CrO_4^{2-} , SeO_4^{2-} , AsO_4^{3-}) where a marked adsorption edge is observed for Mo on model adsorbents, specifically hydrous oxides. The adsorption of MoO_4^{2-} by soils increases with increased ionic strength up to about 0.04 N (Barrow 1974; Gonzalez et al. 1974), possibly reflecting suppression of negatively charged interfacial potential.

The presence of certain competing anions and soil-saturating cations also influences Mo adsorption. Increasing solution concentrations of poorly or weakly adsorbed anions (Cl^- or SO_4^{2-}) does not effect Mo retention, while PO_4^{3-} , which is strongly adsorbed, sharply decreases molybdate adsorption (Barrow 1974; Gonzalez et al. 1974, Karimian and Cox 1978). Additionally, phosphate readily displaces freshly-adsorbed MoO_4^{2-} (Barrow 1974; Gonzalez et al. 1974). Soils saturated with Al^{3+} or Fe^{3+} may adsorb larger quantities of MoO_4^{2-} than the same soils pretreated with Ca^{2+} , NH_4^+ , or K^+ (Pasricha and Randhawa 1977). It appears that adsorbed Fe and Al hydrolyze and may polymerize, thus reducing solution pH and forming hydrous oxide surfaces with high affinity for Mo. In contrast, displacement of exchangeable Al, Fe, and H^+ by K^+ or NH_4^+ negates this effect and reduces Mo retention.

The importance of Fe oxides as a factor in controlling Mo transport in soils is documented in the literature. For example, a soil clay isolate ($<2 \mu\text{m}$) consisting mostly of the layer lattice silicates (kaolinite and illite) has two distinct types of adsorption sites for MoO_4^{2-} (Theng 1971). Following treatment to remove "free" Fe oxides, only one type of site of reduced capacity remains. Similarly, the adsorption capacities of allophanic soil clays for Mo are reduced by removal of Fe oxides (Theng 1971). Adsorption of MoO_4^{2-} by Al_2O_3 , SiO_2 , and soil likely occurs through anion displacement or surface complexation (shown below) with the concomitant release of two hydroxyl ions:



However, adsorption to amorphous Fe oxide between pH 4 and 5 produces 3OH^- groups per MoO_4^{2-} ion adsorbed, probably due to the formation of insoluble iron molybdate (Reisenauer et al. 1962):



Molybdate adsorption in soils becomes increasingly irreversible with prolonged contact time (Barrow 1974), supporting the possibility of a precipitation reaction following adsorption. Further, adsorption of MoO_4^{2-} by hematite, $\alpha\text{-Fe}_2\text{O}_3$, occurs either at two types of sites or by two reactions (Reyes and Jurinak 1967). One reaction is not affected by temperature, whereas the other is endothermic and may be due to adsorbate surface interactions or, perhaps, iron molybdate formation.

Table 17-1. ADSORPTION CONSTANTS FOR MOLYBDENUM

Adsorbent			Adsorbate	Electrolyte		Adsorption Measurements			Reference
Identity (a)	CEC meq/100g	S ₂ A, m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
<u>Soil Clays</u>									
Allophane AB									
untreated	35	291	10 ⁻⁷ - 10 ⁻⁵	NaCl	0.2	5.5	A _m , K _L	27.1, (4.9)	Theng 1971
	35	291	10 ⁻⁷ - 10 ⁻⁵	NaCl	0.2	4.0	A _m , K _L	100, (5.0)	
treated with:									
Dithionite-citrate	-	-	10 ⁻⁷ - 10 ⁻⁵	NaCl	0.2	4.0	A _m , K _L	61.5, (4.8)	
Polyphosphate	-	-	10 ⁻⁷ - 10 ⁻⁵	NaCl	0.2	4.0	A _m , K _L	61.5, (4.8)	
Allophane A									
untreated	49	50	10 ⁻⁷ - 10 ⁻⁵	NaCl	0.2	5.5	A _m , K _L	17.7, (4.5)	
	49	50	10 ⁻⁷ - 10 ⁻⁵	NaCl	0.2	4.0	A _m , K _L	60.5, (4.9)	
treated with:									
Dithionite-citrate	-	-	10 ⁻⁷ - 10 ⁻⁵	NaCl	0.2	4.0	A _m	43.8, (4.7)	
Polyphosphate	-	-	10 ⁻⁷ - 10 ⁻⁵	NaCl	0.2	4.0	A _m	28.2, (4.7)	
Kaolin + Illite	25	130	10 ⁻⁷ - 10 ⁻⁵	NaCl	0.2	5.5	A _m , K _L	8.86, (4.6)	
untreated	25	130	10 ⁻⁷ - 10 ⁻⁵	NaCl	0.2	4.0	A _m , K _L	15.6, (5.1)	
							A _m , K _L	39.1, (4.4)	
<u>Fe Oxides</u>									
α-Fe ₂ O ₃	-	10.4	10 ⁻⁶ - 10 ⁻³	NaMoO ₄	variable	4.0	A _m , K _L	71.7, (5.2)	Reyes and Jurinak 1967
						7.75	A _m	11.75, (5.3)	
Fe ₂ O ₃ ·xH ₂ O(am)	-	-	0 - 10 ⁻⁵	NH ₄ OAc	0.004	4.4- 5.5	K _F , 1/N, B	9550, 0.52, 0.33	Reisenauer et al. 1962
Alumina	-	-	0 - 10 ⁻⁵	NH ₄ OAc	0.004	4.4- 5.5	K _F , 1/N, B	3550, 0.57, 0.50	
Ti Oxide	-	-	0 - 10 ⁻⁵	NH ₄ OAc	0.004	4.4- 5.5	K _F , 1/N, B	1900, 0.45, 0.50	

Table 17-1 (Contd). ADSORPTION CONSTANTS FOR MOLYBDENUM

Adsorbent				Adsorbate		Electrolyte			Adsorption Measurements		Reference
Identity (a)		CEC meq/100g	S.A. m ² /g	Conc., M		Identity	Conc., M	pH	Constants (b)	Value (c)	
Soils	% O.C.	% Free Fe						Soil water/ 1N KCl			
	5.2	0.17	-	-	10 ⁻⁴ - 10 ⁻³	-	-	5.4/4.5	K _F , 1/N	0.815, 1.21	Karimian and Cox 1978
	38.6	0.25	-	-	10 ⁻⁴ - 10 ⁻³	-	-	4.9/3.9	A _m , K _L K _F , 1/N	3.49, 4.38 0.429, 0.320	
	66.0	0.24	-	-	10 ⁻⁴ - 10 ⁻³	-	-	4.7/4.2	A _m , K _L K _F , 1/N	8.68, 4.04 1.54, 0.584	
	81.3	0.4	-	-	10 ⁻⁴ - 10 ⁻³	-	-	3.4/2.4	K _F , 1/N	16.9, 0.905	
	1.8	0.32	-	-	10 ⁻⁴ - 10 ⁻³	-	-	5.5/5.2	K _F , 1/N	0.307, 1.07	
	0.7	0.14	-	-	10 ⁻⁴ - 10 ⁻³	-	-	5.6/5.2	K _F , 1/N	0.228, 0.918	
	2.1	5.4	-	-	10 ⁻⁴ - 10 ⁻³	-	-	5.3/4.8	A _m , K _L K _F , 1/N	8.63, 4.11 1.23, 0.459	
	0.6	0.57	-	-	10 ⁻⁴ - 10 ⁻³	-	-	5.8/4.1	A _m , K _L K _F , 1/N	4.46, 3.66 0.481, 0.571	
Skaggs			-	-	0 - 10 ⁻⁵	NH ₄ OA	0.004	4.4-5.5	K _F , 1/N, B	300, 0.51, 0.50	Reisenauer et al. 1962
Cornlong			-	-	0 - 10 ⁻⁵	NH ₄ OAc	0.004	4.4-5.5	K _F , 1/N, B	95, 0.48, 0.50	
Chaml sal			-	-	0 - 10 ⁻⁵	NH ₄ OAc	0.004	4.4-5.5	K _F , 1/N, B	99, 0.64, 0.50	

Table 17-1 (Contd). ADSORPTION CONSTANTS FOR MOLYBDENUM

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		Reference
Identity (a)	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
<u>Soils</u>									
Loam Untreated	-	-	10 ⁻⁴ - 10 ⁻³	-	-	5.9-6.2	K _F , 1/N, a _m , K _L	(0.48, 0.12, 1.06, 4.8)	Pasricha and Randhawa 1977
K-saturated	-	-	10 ⁻⁴ - 10 ⁻³	-	-	6.5-6.6	K _F , 1/N	(0.008, 0.89)	
NH ₄ -saturated	-	-	10 ⁻⁴ - 10 ⁻³	-	-	6.0-6.6	K _F , 1/N	(0.003, 1.01)	
Ca-saturated	-	-	10 ⁻⁴ - 10 ⁻³	-	-	6.0-6.2	K _F , 1/N, A _m , K _L	(0.16, 0.45, 2.64, 4.0)	
Al-saturated	-	-	10 ⁻⁴ - 10 ⁻³	-	-	3.8-4.9	K _F , 1/N, A _m , K _L	(0.69, 0.37, 4.00, 4.9)	
Fe-saturated	-	-	10 ⁻⁴ - 10 ⁻³	-	-	4.7-5.5	K _F , 1/N, A _m , K _L	(1.14, 0.44, 1.77, 5.8)	
Sand Loam Untreated	-	-	10 ⁻⁴ - 10 ⁻³	-	-	6.6-6.7	K _F , 1/N A _m , K _L	(0.011, 0.90 14.9, 2.7)	
K-saturated	-	-	10 ⁻⁴ - 10 ⁻³	-	-	7.2-7.5	K _F , 1/N, A _m , K _L	(0.009, 0.82, 3.56, 3.2)	
NH ₄ -saturated	-	-	10 ⁻⁴ - 10 ⁻³	-	-	7.0	K _F , 1/N	(0.002, 1.17)	
Ca-saturated	-	-	10 ⁻⁴ - 10 ⁻³	-	-	6.6-6.9	K _F , 1/N	(0.00, 1.86)	
Al-saturated	-	-	10 ⁻⁴ - 10 ⁻³	-	-	4.2-5.2	K _F , 1/N, A _m , K _L	(0.39, 0.33, 2.80, 4.5)	
Fe-saturated	-	-	10 ⁻⁴ - 10 ⁻³	-	-	5.1-5.5	K _F , 1/N A _m , K _L	(0.76, 0.37 4.11, 5.1)	

Table 17-1 (Contd). ADSORPTION CONSTANTS FOR MOLYBDENUM

Adsorbent			Adsorbate		Electrolyte			Adsorption Measurements		Reference	
Identity (a)			CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
Soils	% Free Fe	% Free Al						Soil			
	5.2	1.2	16.1	-	10 ^{-3.7} - 10 ^{-2.7}	None	-	4.2	A _m , K _L	(12.6, 5.0)	Barrow 1972
						CaCl ₂	0.002	-	A _m , K _L	(13.2, 5.8)	
						CaCl ₂	0.005	-	A _m , K _L	(20.3, 5.6)	
						CaCl ₂	0.01	-	A _m , K _L	(17.4, 5.8)	
						CaCl ₂	0.02	-	A _m , K _L	(18.6, 5.7)	
	0.8	0.3	10.3	-	10 ^{-4.5} - 10 ^{-3.7}	None	-	5.2	A _m , K _L	(0.71, 5.1)	
						CaCl ₂	0.002	-	A _m , K _L	(1.15, 5.5)	
						CaCl ₂	0.005	-	A _m , K _L	(1.15, 5.5)	

						CaCl ₂	0.01	-	A _m , K _L	(2.20, 5.5)
						CaCl ₂	0.02	-	A _m , K _L	(2.02, 5.4)
	2.1	0.5	26.3	-	10 ⁻⁵ - 10 ^{-4.1}	None	-	6.2	A _m , K _L	(0.47, 5.1)
						CaCl ₂	0.002	-	A _m , K _L	(0.98, 5.1)
						CaCl ₂	0.005	-	A _m , K _L	(0.75, 5.4)
						CaCl ₂	0.01	-	A _m , K _L	(1.12, 5.2)
						CaCl ₂	0.02	-	A _m , K _L	(0.90, 5.4)
Sol I	-	-			10 ^{-4.7} - 10 ^{-3.2}	CaCl ₂	0.01	-	A _m , K _L	(0.38, 5.6)
	-	-			10 ^{-4.7} - 10 ^{-3.2}	CaCl ₂	0.01	-	A _m , K _L	(1.64, 5.3)
	-	-			10 ^{-4.7} - 10 ^{-3.2}	CaCl ₂	0.01	-	A _m , K _L	(1.67, 6.3)
	-	-			10 ^{-4.7} - 10 ^{-3.2}	CaCl ₂	0.01	-	A _m , K _L	(2.82, 5.8)
	-	-			10 ^{-4.7} - 10 ^{-3.2}	CaCl ₂	0.01	-	A _m , K _L	(4.46, 5.7)
	-	-			10 ^{-4.7} - 10 ^{-3.2}	CaCl ₂	0.01	-	A _m , K _L	(4.66, 6.0)

Barrow 1970

Table 17-1 (Contd). ADSORPTION CONSTANTS FOR MOLYBDENUM

Adsorbent			Adsorbate		Electrolyte			Adsorption Measurements		Reference	
Identity ^(a)			CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants ^(b)	Value ^(c)	
<u>Soils</u>											
Org. C, %	Free Fe, %	Allophane, %									
10.7	2.6	15.1	-	-	10 ⁻³ - 10 ⁻²	-	-	6.0	A _m , K _L , K _S	62.3, 2.23, (3.9)	Gonzalez et al. 1974
11.4	2.9	16.0	-	-	10 ⁻³ - 10 ⁻²	-	-	6.1	A _m , K _L , K _S	59.5, 2.32, (3.8)	
11.2	5.1	21.4	-	-	10 ⁻³ - 10 ⁻²	-	-	6.1	A _m , K _L	105, 2.66	
11.3	4.3	16.5	-	-	10 ⁻³ - 10 ⁻²	-	-	6.0	A _m , K _L	93.7, 2.69	
6.2	5.6	27.4	-	-	10 ⁻³ - 10 ⁻²	-	-	5.6	A _m , K _L	114, 3.19	
6.0	6.5	6.2	-	-	10 ⁻³ - 10 ⁻²	-	-	5.2	A _m , K _L , K _S	37.0, 3.10, (9.5)	
4.6	6.4	9.8	-	-	10 ⁻³ - 10 ⁻²	-	-	5.3	A _m , K _L , K _S	38.0, 3.28, (7.4)	
1.4	6.4	13.6	-	-	10 ⁻³ - 10 ⁻²	-	-	5.5	A _m , K _L , K _S	104, 2.76, (3.3)	
14.9	4.7	17.6	-	-	10 ⁻³ - 10 ⁻²	-	-	5.3	A _m , K _L , K _S	52.1, 3.25, (9.3)	
5.3	6.3	25.1	-	-	10 ⁻³ - 10 ⁻²	-	-	5.7	A _m , K _L , K _S	133, 2.93, (3.7)	
4.5	7.1	24.0	-	-	10 ⁻³ - 10 ⁻²	-	-	6.0	A _m , K _L , K _S	170, 2.99, (8.2)	
29.5	2.3	12.7	-	-	10 ⁻³ - 10 ⁻²	-	-	5.3	A _m , K _L	25.1, 3.27	
10.7	5.8	25.2	-	-	10 ⁻³ - 10 ⁻²	-	-	5.9	A _m , K _L	92.6, 2.95	
7.0	4.5	24.3	-	-	10 ⁻³ - 10 ⁻²	-	-	5.5	A _m , K _L	100, 3.09	
5.6	5.0	20.4	-	-	10 ⁻³ - 10 ⁻²	-	-	5.8	A _m , K _L	109, 3.07	
8.0	5.8	20.4	-	-	10 ⁻³ - 10 ⁻²	-	-	6.0	A _m , K _L	198, 2.99	

(a) O.C. = organic carbon

(b) A_m = Langmuir adsorption maximum, $\mu\text{mol g}^{-1}$ A_m, A₁ = two adsorption sitesK_F, 1/N = Freundlich constantsK_L = Langmuir constant, $\log \frac{M}{1/N} + B$ B = constant for A = K_FC^{1/N} [H⁺]^B, variation of Freundlich equation with pHK_S = selectivity coefficient, PO₄²⁻ over MoO₄²⁻

(c) () = estimated values

Section 18

NICKEL

Nickel (Ni) in natural aqueous environments exist as +2 valence state. NiFe_2O_4 under oxidizing conditions is predicted to be the most stable among compounds for which thermodynamic data are available. Although Ni^{2+} forms fairly strong complexes with SO_4^{2-} , Ni^{2+} is expected to be the primary species at low SO_4^{2-} levels expected in utility waste environment. Attenuation mechanisms of Ni have not been extensively studied. Limited data suggests that NiFe_2O_4 under oxidizing and NiS under reducing conditions may be important solubility-controlling solids. The relative importance of ion exchange and specific adsorption of Ni has not been established. Nickel is strongly, and possibly irreversibly, adsorbed by alkaline soils. Cations, such as Ca^{2+} and Mg^{2+} , have been reported to reduce Ni adsorption, through competition for Ni adsorption sites. Anions, such as SO_4^{2-} , reduce adsorption through reduction in Ni^{2+} activity as a result of complexation.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIES

In natural aqueous environments, the +2 valence state of nickel is of primary importance. Nickel forms several compounds with different ligands such as OH^- , SO_4^{2-} , CO_3^{2-} , PO_4^{3-} , and S^{2-} . Of these compounds Ni ferrite (NiFe_2O_4) is the most stable compound under oxidizing conditions. The compounds of OH^- , SO_4^{2-} , and of S^{2-} (in oxidizing conditions) are very soluble, and the stability of millerite (NiS) increases with the decrease in redox potential. NiCO_3 and Ni(OH)_2 have relatively fast precipitation kinetics but the solubility product of Ni(OH)_2 is considerably lower than that of NiCO_3 ; thus, NiCO_3 is not expected to be stable in geologic environments.

To determine the relative abundance of Ni(II) species in ground waters representative of leachates, activities of different Ni species [Ni^{2+} fixed at 10^{-7} M or controlled by Ni(OH)_2] were plotted (Figure 18-1) using the thermodynamic data (Truesdell and Jones 1974, Ball et al. 1980) contained in the geochemical model MINTEQ (Felmy et al. 1983). Under the assumed conditions (Figure 18-1), Ni^{2+} followed by NiSO_4^0 is the dominant aqueous species in ground waters of pH values <9.0. For a short pH interval (pH ~9.2 to 9.8), NiHCO_3^+ appears to be dominant. At

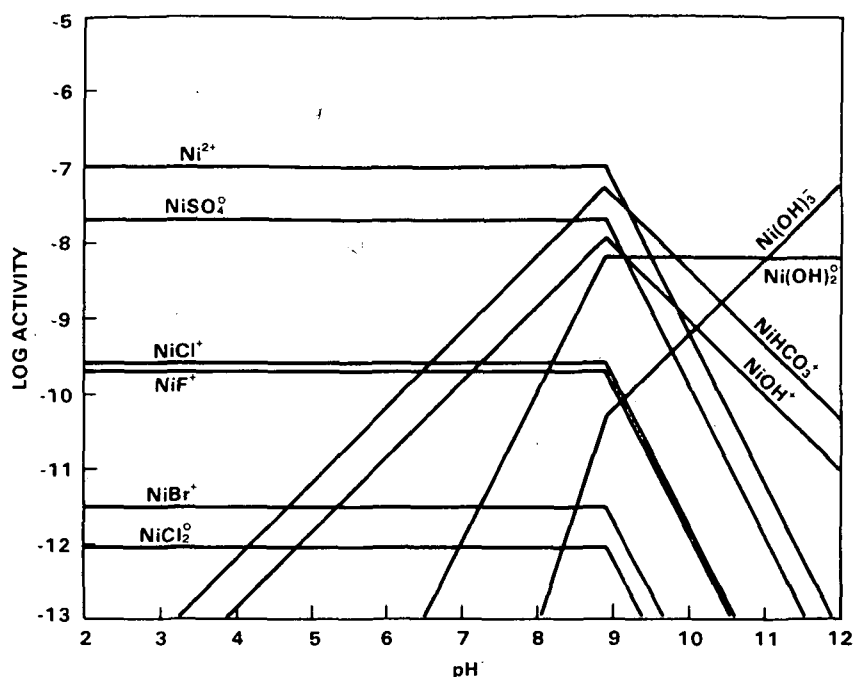


Figure 18-1. Activities of Different Ni^{2+} species when activities of Ni^{2+} Fixed at 10^{-7} or Controlled by $\text{Ni}(\text{OH})_2$, $\text{SO}_4^{2-} = \text{Cl}^- = 10^{-3}$, $\text{F}^- = 10^{-4}$, $\text{Br}^- = 10^{-5}$, and $\text{CO}_2(\text{gas}) = 10^{-3.52}$ Atmosphere.

pH values of ~ 9.8 , hydrolysis species $[\text{Ni}(\text{OH})_2^0, \text{Ni}(\text{OH})_3]$ appear dominant. However, the thermodynamic data for hydrolysis species used by Ball et al. (1980) is from Baes and Mesmer (1976) and the latter authors report that the values for $\text{Ni}(\text{HO})_2^0$ and $\text{Ni}(\text{OH})_3$ are uncertain. Other Ni complexes (NiCl^+ , NiF^+ , NiBr^+) do not contribute significantly to the total Ni in solution.

PRECIPITATION/DISSOLUTION

Precipitation/dissolution of Ni compounds in natural environments has not been extensively studied. Hem (1977) used thermodynamic data to predict that NiFe_2O_4 might control Ni^{2+} concentrations in natural systems. Sadiq and Zaidi (1981) supported this prediction with observations of Ni^{2+} on hydrous iron oxide. The concentrations of Ni^{2+} were similar to those expected in equilibrium with NiFe_2O_4 . Theis and Richter (1980) measured Ni^{2+} adsorption on SiO_2 (quartz) and $\alpha\text{-FeOOH}$ (goethite). They determined that $\text{Ni}(\text{OH})_2(\text{am})$ was not the solubility-controlling solid. However, NiFe_2O_4 is less soluble than $\text{Ni}(\text{OH})_2(\text{am})$, and Theis and Richter (1980) did not consider NiFe_2O_4 as the solubility-controlling solid. However, Theis and Richter's data show that the amount of Ni^{2+} adsorbed by goethite is larger than

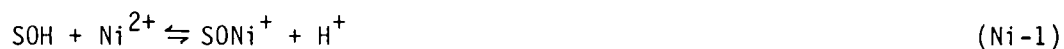
that adsorbed by quartz and that the pattern of adsorption is consistent with the possible formation of NiFe_2O_4 . Bowman et al. (1981) observed partially irreversible adsorption in basic soils, which suggests the formation of Ni solid phases.

NiS will only be stable in aqueous environments under reducing conditions. NiS has been calculated to be the solubility-controlling solid for deep ground waters (E. A. Jenne, Personal communication, April, 1983, based on unpublished data, Pacific Northwest Laboratory, Richland, Washington).

ADSORPTION/DESORPTION

The adsorptive behavior of Ni in soil has not been extensively investigated. Limited studies suggest that Ni may be strongly adsorbed by soil (Wangen et al. 1982, Bowman et al. 1981). Nickel is specifically adsorbed by Fe and Mn oxides (McKenzie 1980, Murray 1975, Jenne 1968). The specific adsorption affinity is less than that of Pb, Cu, and Zn (McKenzie 1980, Murray 1975) but may exceed that of Cd (Wangen et al. 1982). It is reasonable to assume that, like other cationic metals, Ni adsorption in soils will be controlled by aqueous hydrolysis, specific adsorption, and ion exchange. Thus, iron and manganese oxides, and to a lesser extent, clay minerals are the most important adsorbents. This supposition is supported, in part, by available literature (Bowman et al. 1981, Artiola and Fuller 1980, Sadiq and Zaidi 1981). Organic material, though of presumed importance (Kerndorff and Schnitzer 1980), has not been identified as an important adsorbent of Ni in soil.

Nickel adsorption is pH dependent (Table 18-1) on silica (Theis and Richter 1980), iron oxides (Theis and Richter 1980; McKenzie 1980), and manganese oxides (McKenzie 1980; Murray 1975). In the absence of strong complexing ligands the adsorption edge ranges from pH 5.5 to 8.5 depending on the adsorbent and experimental conditions. The adsorption of Ni releases approximately 1 to 1.5 moles H^+ for each mole of Ni adsorbed by iron oxide (Theis and Richter 1980; Kinniburgh et al. 1976; McKenzie 1980) and Mn oxides (Murray 1975); as many as 2.3 protons are released for each Ni species adsorbed by Al oxides (Kinniburgh et al. 1976). These data indicate that while Ni^{+2} is the predominant solution species of Ni below pH 8 (Mattigod et al. 1979; Theis and Richter 1980; Figure 18-1), NiOH^+ is preferentially adsorbed, perhaps forming both mono- and bi-dentate surface complexes:





Thermodynamic calculations (Koppelman and Dillard 1977) and ion speciation studies (Mattigod et al. 1979; Bowman and O'Conner 1982) indicate that Ni^{2+} (see Figure 18-1) is the primary adsorbing species for clay minerals.

Competing cations and complexing ligands may significantly influence Ni adsorption by soils and model adsorbents (Table 18-1). Increasing ionic strength with NaCl, NaClO_4 , NaNO_3 , CaCl_2 , $\text{Ca}(\text{ClO}_4)_2$ or $\text{Ca}(\text{NO}_3)_2$ reduces Ni adsorption by clays (Mattigod et al. 1979) and soils (Bowman et al. 1981; Doner et al. 1982). Cationic competition for adsorption sites and decreasing solution activity of Ni^{2+} are possible explanations for this phenomenon. A greater reduction in adsorption is observed when Ca^{2+} is the major cation, suggesting it is a more effective competitor with Ni. Competitive adsorption experiments have not been performed with other cationic metals. However, similarities in apparent adsorption chemistry suggest that Zn and Cd may compete with Ni for specific adsorption sites on some oxides of Fe and Al (Benjamin and Leckie 1980). The addition of sulfate (Mattigod et al. 1979; Theis and Richter 1980; Bowman and O'Conner 1982), citrate (Theis and Richter 1980), nitrilo-triacetate (Theis and Richter 1980) and EDTA (Bowman et al. 1981) reduces the adsorption of Ni by clay minerals (Mattigod et al. 1979; Bowman and O'Connor 1982), silica and goethite (Theis and Richter 1980) and soil (Bowman et al. 1981) through formation of aqueous complexes with Ni^{2+} . Formation of the strongly adsorbing species, NiOH^+ , is also hindered by complex formation. While glycine and cyanide also suppress the adsorption of Ni^{2+} and NiOH^+ by goethite, specific adsorption of Ni-complexes of these ligands occurs to a small extent (Theis and Richter 1980).

Limited studies indicate that the kinetics of Ni desorption from near-neutral and basic soils may be slow (Bowman et al. 1981). This partially irreversible adsorption may indicate formation of an insoluble Ni solid phase which may further limit the transport of Ni in the subsurface environment. In contrast, Ni adsorbed by goethite (pH 5.5) and kaolinite (pH 6.3) is desorbable with comparable kinetics to adsorption (Wangen et al. 1982).

Table 18-1. ADSORPTION CONSTANTS FOR NICKEL

Adsorbent			Adsorbate		Electrolyte		Adsorption Measurements		Reference
Identity (a)	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
<u>Clay Minerals</u>									
Kaolinite, Ca-saturated	11.7	-	10 ^{-5.7} - 10 ^{-4.8}	Ca(NO ₃) ₂	0.005	-	a,b	0, 0.058	Mattigod et al. 1979
				"	0.001		a,b	0, 0.045	
				"	0.025		a,b	0, 0.036	
				"	0.375		a,b	-0.040, 0.034	
				"	0.005-0.375		a,b ¹	0.735 × 10 ³	
Na-saturated	11.7	-	10 ^{-5.7} - 10 ^{-4.8}	CaSO ₄	0.002, 0.005		a,b ¹	0.028, 10.4 × 10 ³	
				NaNO ₃	0.01, 0.1		a,b ¹	0, 185 × 10 ³	
				Na ₂ SO ₄	0.003, 0.05		a,b ¹	0.062, 59.5 × 10 ³	
				-	-		ΔG ⁰ _{ads}	-6.5	
Montmorillonite	-	-	10 ^{-6.5}	Seawater	~0.7	8	K _d	0.2	Takematsu 1979
Reductant-treated red clay	-	-	10 ^{-6.5}	Seawater	~0.7	8	K _d	0.2	
Chlorite	16	14	10 ^{-2.8}	-	-	6.7	A	61.3	Koppelman and Dillard 1977
Illite	20	49	10 ^{-2.8}	-	-	6.2	"	40.9	
Kaolinite	7	12	10 ^{-2.8}	-	-	5.1	"	6.8	
<u>Silica</u>									
αSiO ₂	-	1.7	10 ^{-4.8}	NaClO ₄	0.01	8.3	A	(0.29)	Thels and Richter 1980
				+Citrate	10 ⁻⁵	"	"	(0.13)	
				+NTA	10 ⁻⁶	"	"	(0.27)	
				+NTA	10 ⁻⁵	"	"	(0.12)	
				+Glycine	10 ⁻⁵	"	"	(0.25)	
				+Glycine	10 ⁻⁴	"	"	(0.09)	
				+CN ⁻	10 ⁻⁵	"	"	(0.10)	
						"	ΔG ⁰ _{chem}	-6.55	

Table 18-1 (Contd). ADSORPTION CONSTANTS FOR NICKEL

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		Reference
Identity (a)	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
<u>Alumina</u>									
Fresh Al oxide gel	-	-	10 ^{-3.9}	NaNO ₃	1.0	6.3	A	(8.6)	Kinniburgh et al. 1976
<u>Fe Oxides</u>									
Goethite	-	85	10 ^{-4.8}	NaClO ₄	0.01	6.5	A	(14.4)	Thels and Richter 1980
				+ SO ₄ ²⁻	0.1			(11.5)	
				+ Citrate	10 ⁻⁵			(8.1)	
				+ Citrate	10 ⁻⁴			(6.0)	
				+ NTA	10 ⁻⁵			(6.9)	
				+ CN ⁻	10 ⁻⁵			(6.9)	
							ΔG _{chem} ^o	-5.35	
Fresh Fe oxide gel	-	-	10 ^{-3.9}	NaNO ₃	1.0	5.6	A	(8.6)	Kinniburgh et al. 1976
Hydrated Fe oxide	-	-	10 ^{-6.5}	Seawater	~0.7	8	K _d	100	Takematsu 1979
Goethite (α-FeOOH)	-	75	10 ^{-4.4}	KNO ₃	0.1	6.0	A	(10)	McKenzie 1980
Hematite (α-Fe ₂ O ₃)	-	20	10 ^{-4.4}	KNO ₃	0.1	6.8	A	(10)	
<u>Mn Oxides</u>									
α-Mn ₂ O ₃	-	-	0.1	Cl ⁻	0.1	5.2	A	(15)	McKenzie 1972
γ-MnOOH	-	-	0.1	Cl ⁻	0.1	5.6	A	(30)	
Mn ₃ O ₄	-	-	0.1	Cl ⁻	0.1	6.1	A	(98)	
δ-MnO ₂	-	98	10 ⁻³ - 10 ^{-2.2}	KNO ₃	0.1	5	A _m , K _L	(690, 3.6)	McKenzie 1980
α-MnO ₂ (K ₂ Mn ₈ O ₁₆)	-	206	10 ⁻³ - 10 ^{-2.2}	KNO ₃	0.1	5	A _m , K _L	(500, 3.4)	

Table 18-1 (Contd). ADSORPTION CONSTANTS FOR NICKEL

Adsorbent			Adsorbate		Electrolyte			Adsorption Measurements		Reference	
Identity (a)	CEC meq/100g	S ₂ A ₂ m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)			
<u>Mn Oxides (contd)</u>											
α-MnOOH	-	-	10 ^{-6.5}	Seawater	~0.7	8	K _d	10	Takematsu 1979		
7Å MnO ₂	-	-	10 ^{-6.5}	Seawater	~0.7	8	K _d	40			
δ-MnO ₂	-	-	10 ^{-6.5}	Seawater	~0.7	8	K _d	300			
<u>Organic Matter</u>											
Humic acid	-	-	10 ^{-5.3} - 10 ^{-3.3}	-	-	2.4	A _m , K _d	(9.2, 4.0)	Kerndorff and Schnitzer 1980		
			10 ^{-3.3}	-	-	6.0	A	(125)			
<u>Soil</u>	<u>% Clay</u>	<u>% O.C.</u>	<u>Soil</u>								
Silt loam	25	1.0	16.2	59.8	10 ^{-6.8} - 10 ^{-3.8}	CaCl ₂	0.01	6.1	K _F , 1/N	0.30, 0.95	Bowman et al. 1981
						"	0.1	"	"	0.057, 0.91	
						Ca(ClO ₄) ₂	0.1	"	"	0.083, 0.94	
					10 ^{-3.8} - 10 ^{-1.8}	CaCl ₂	0.01	"	"	0.27, 0.57	
Sandy loam	10.0	0.45	5.5	11.4	10 ^{-6.8} - 10 ^{-3.8}	CaCl ₂	0.01	6.5	K _F , 1/N	0.11, 0.87	
Loamy sand	3.4	0.17	1.6	0.51	10 ^{-6.8} - 10 ^{-3.8}	CaCl ₂	0.01	6.7	K _F , 1/N	0.010, 0.92	
						"	0.1	"	"	0.005, 0.87	
						Ca(ClO ₄) ₂	0.1	"	"	0.007, 0.87	
Sand	5.0	0.02	6.2	11.2	10 ^{-6.8} - 10 ^{-3.8}	CaCl ₂	0.01	8.2	K _F , 1/N	0.31, 1.18	
Sand	7.7	0.04	8.1	10.9	10 ^{-6.8} - 10 ^{-3.8}	CaCl ₂	0.01	7.9	K _F , 1/N	0.50, 1.02	
Sand	5.6	0.04	7.8	14.6	10 ^{-6.8} - 10 ^{-3.8}	CaCl ₂	0.01	8.4	K _F , 1/N	0.37, 1.01	
Clay	57.0	0.97	35.2	177	10 ^{-6.8} - 10 ^{-3.8}	CaCl ₂	0.01	7.6	K _F , 1/N	0.60, 1.03	
						"	0.1	"	"	0.62, 0.95	
						Ca(ClO ₄) ₂	0.1	"	"	0.73, 0.98	
Clay loam	27.3	1.1	18.5	65.9	10 ^{-6.8} - 10 ^{-3.8}	CaCl ₂	0.01	8.1	K _F , 1/N	0.51, 1.02	

Table 18-1 (Contd). ADSORPTION CONSTANTS FOR NICKEL

Adsorbent					Adsorbate		Electrolyte		Adsorption Measurements		Reference
Identity (a)		CEC meq/100g	S ₂ A. m/g		Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
Soil	% Clay % O.C.										
Silt loam	27.0 1.5	19.0	71.6	10 ^{-6.8} - 10 ^{-3.8}	CaCl ₂	0.01		5.9	K _F , 1/N	0.44, 0.96	
Sandy loam	14.0 0.45	10.9	46.2	10 ^{-6.8} - 10 ^{-3.8}	CaCl ₂	0.01		7.6	K _F , 1/N	0.20, 0.99	Bowman et al. 1981
					"	0.1		7.6	K _F , 1/N	0.13, 0.81	
					Ca(ClO ₄) ₂	0.1		7.6	K _F , 1/N	0.15, 0.85	
Sandy loam	13.7 0.43	14.0	64.9	10 ^{-6.8} - 10 ^{-3.8}	CaCl ₂	0.01		7.7	K _F , 1/N	0.25, 0.98	
Sandy loam	14.4 0.57	14.1	65.6	10 ^{-6.8} - 10 ^{-3.8}	CaCl ₂	0.01		7.8	K _F , 1/N	0.48, 0.97	
<u>Soil</u>											
	51 -	9	51.3	10 ^{-4.5}	municipal	-		5.4	PV, CL	(3.1, 0.8)	Artiola and Fuller 1980
	31 -	19	61.5	10 ^{-4.5}	solid waste	-		5.4	PV, CL	(5.2, 1.4)	
	15 -	6	19.8	10 ^{-4.5}	leachate	-		5.4	PV, CL	(3.0, 0.4)	
	11 -	10	38.3	10 ^{-4.5}	"	-		5.4	PV, CL	(6.4, 1.2)	
	8 -	10	8.9	10 ^{-4.5}	"	-		5.4	PV, CL	(1.9, 0.14)	
	4 -	2	8.0	10 ^{-4.5}	"	-		5.4	PV, CL	(0.6, 0.1)	
Sandy loam	- 0.3	5	-	10 ^{-3.8}	NaCl	0.1		6.7	PV, CL	(125, 2.1)	Doner et al. 1982
					"	0.5		6.5	"	(65, 0.9)	
					NaClO ₄	0.1		6.7	"	(135, 2.2)	
					"	0.5		6.2	"	(87, 1.3)	

(a) O.C. = organic carbon

(b) a, b ≡ Intercept, slope of linear isotherm, $y = a + bx$; $y = \mu\text{mol g}^{-1}$; $x = [\text{Ni}^{2+}]_{\text{eq}} \ln \mu\text{M}$
b' ≡ slope where $x = \text{Ni}^{2+}$ activity $\Delta G_{\text{ADS}}^{\circ}$ = free energy of adsorption, kcal mol^{-1} K_d = distribution coefficient, L g^{-1} A = adsorption, $\mu\text{mol g}^{-1}$ A_m = Langmuir adsorption maximum, $\mu\text{mol g}^{-1}$ K_L = Langmuir constant, $\log \text{M}^{-1}$ $K_F, 1/N$ = Freundlich constants for $A = K_F C^{1/N}$; A , $\mu\text{mol g}^{-1}$; C , μM

PV = pore volumes to 50% breakthrough

CL = column loading, $\mu\text{mol g}^{-1}$

(c) () = estimated values

Section 19

SELENIUM

Selenium (Se) exists in natural aqueous environments in -2, +4, and +6 valence states. Most of the Se species in the environmental Eh and pH range (4 to 10) exist as anions. Although some of the studies indicate precipitation may occur, no definitive information on solubility-controlling solids is available. Maximum adsorption of selenate and selenite occurs primarily through specific adsorption in the acidic pH range on geologic materials enriched in hydrous oxides of Al and Fe or amorphous aluminosilicates. Sulfate is reported to compete for Se adsorption sites.

RELATIVE STABILITY OF SOLID AND SOLUTION SPECIES

Selenium is a multivalent element and can exist in -2, 0, +4, +6 valence states. In aqueous environments, however, it exists in -2, +4 and +6 states. Using the selected thermodynamic data (Table A-8), stability fields for various Se solution species were calculated as a function of redox potential (pe) and pH (Figure 19-1). Under reducing conditions, H_2Se^0 would dominate below pH 3.8 and HSe^- would dominate above pH 3.8. The selenite species would predominate under intermediate-to-slightly oxidizing conditions. H_2SeO_3 would be the major solution species when $\text{pH} < 2.9$, HSeO_3^- when $2.9 < \text{pH} < 8.4$, and SeO_3^{2-} when $\text{pH} > 8.4$. Highly oxidizing conditions ($\text{pe} + \text{pH} \geq 15$) are necessary for SeO_4^{2-} to form to a significant extent.

To determine the relative solubility of the solid phases (see Table A-8) at various redox potentials, Figures 19-2 and 19-3 were developed. The calculated activities of the dominant solution species (HSe^-), under the assumed conditions, show that FeSe_2 is the least soluble among the solid phases reported in Figure 19-2. Solid phases in order of increasing solubility are FeSe_2 , FeSe , CuSe , and Se(c) . If an Fe oxide less soluble than $\text{Fe(OH)}_3(\text{am})$ were chosen to control Fe^{2+} activity, then the solubilities of FeSe_2 and FeSe would increase. However, the solubility product for FeSe_2 is not well defined and the value of K_{sp} yielding the most soluble form is given in Table A-8. The K_{sp} values for CuSe and FeSe were experimentally determined and "confirmed" by numerical approximation (Buketov et al. 1964), but the values are still subject to errors of approximately ± 2.0 orders of magnitude.

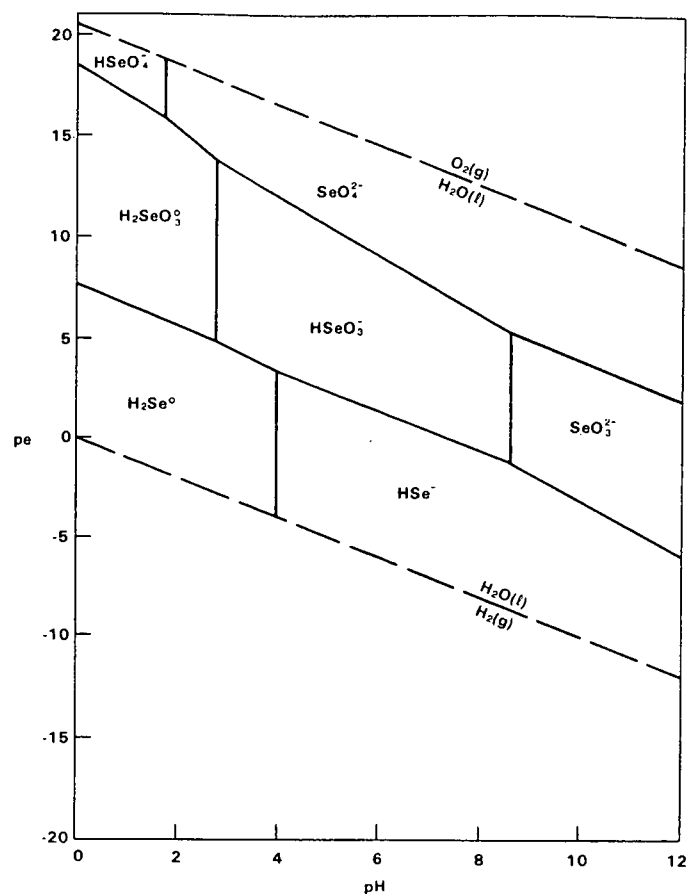


Figure 19-1. pe - pH diagram for $Se - H_2O$ system, at $25^\circ C$. Dashed Lines represent the upper and lower stability limits of water.

Figure 19-3 represents the solubility of Se solids as a function of pH at $pe + pH = 10$. As before, $Fe(OH)_3(am)$ was assumed to control Fe^{2+} activity. $Se(c)$ is by far the least soluble phase. The ferric selenities $[Fe_2(SeO_3) \cdot 2H_2O$ and $Fe_2(OH)_4SeO_3]$ are much more soluble than $Se(c)$. The solubility product value of $Fe_2(OH)_4SeO_3$ is a crude estimate and the stoichiometry of this compound is not known with certainty (Williams and Byers 1936). However, the similarity in solubility between $Fe_2(OH)_4SeO_3$ and $Fe_2(SeO_3)_3 \cdot 2H_2O$ indicates that the two compounds may be the same phase.

Figure 19-4 was constructed to show the effect of continuous change in redox ($pe + pH$) on the solubilities of the least soluble solid phases discussed above. $FeSe_2$ is predicted to control Se solubility up to $pe + pH \approx 6.8$. Beyond $pe + pH 6.8$, $Se(c)$ is predicted to control Se solution concentrations. Above $pe + pH = 7.5$, $HSeO_3^-$

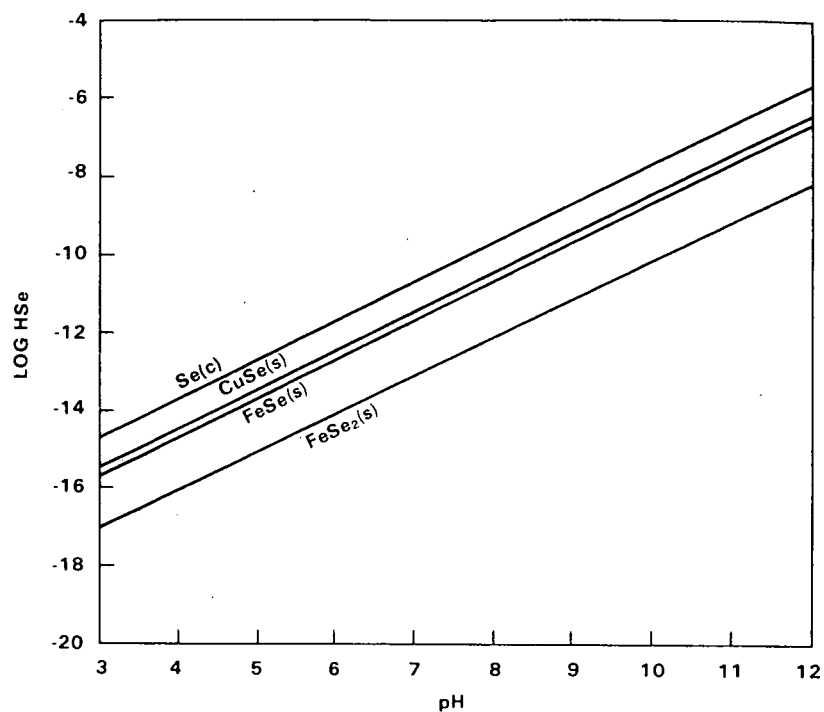


Figure 19-2. Relative solubility of Se solids at $pe + pH = 5$ and in equilibrium with $Fe(OH)_3(am)$ and $\alpha-Cu_2Fe_2O_4$.

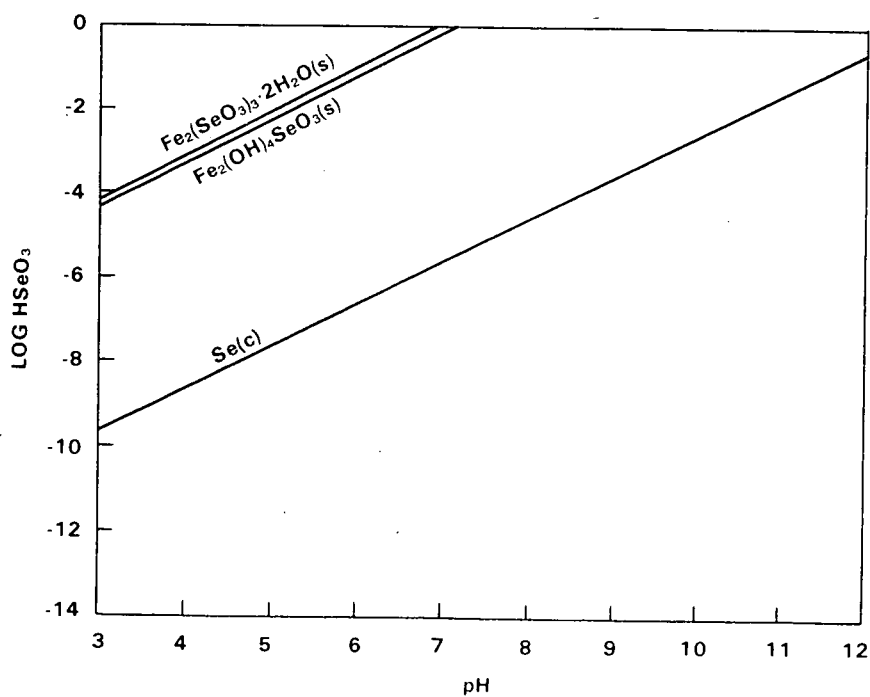


Figure 19-3. Relative solubility of Se solids at $pe + pH = 10$ and in equilibrium with $Fe(OH)_3(am)$.

rather than HSe^- dominates. At this redox potential ($\text{pe} + \text{pH} = 7.5$), Se(c) solubility increases dramatically with increasing redox potential. The solubilities of $\text{Fe}_2(\text{SeO}_3)_3 \cdot 2\text{H}_2\text{O}$ and the selenates at $\text{pe} + \text{pH} > 12.5$ are very high. As a result they are unlikely to form under environmental levels of Se.

PRECIPITATION/DISSOLUTION

Although several solid phases [such as Se(c) , FeSe_2] are predicted to be stable under relatively reducing conditions (see above) and some of the studies indicate precipitation may be occurring, no definitive information on solubility-controlling solids is available. $\text{Fe}_2(\text{OH})_4(\text{SeO}_3)$ was proposed (Gerring et al. 1968) to help explain the insolubility of Se in soils as well as the strong association of Se with Fe in precipitates. Benjamin and Bloom (1981) observed that metal ion adsorption onto amorphous iron oxyhydroxide was enhanced in the presence of adsorbed Se. It was postulated that the enhanced metal adsorption was the result of the formation of an Fe-Se solid phase on the oxyhydroxide surface. Hingston et al. (1974) and Hamdy and Gissel-Nelson (1977) gave indirect evidence of the formation of Se solids. Both groups of researchers observed that selenite was irreversibly adsorbed on crystalline iron oxide surfaces (goethite, hematite), which is an indication of the possible formation of a solid phase.

ADSORPTION/DESORPTION

Selenium retention in soil has not been studied extensively. Limited studies indicate that in spite of their anionic nature, selenite [Se(IV)] and selenate [Se(VI)] may be adsorbed significantly by some soils. The experimental evidence suggests that cryptocrystalline and amorphous forms of SiO_2 , Al_2O_3 , and Fe_2O_3 control Se adsorption (John et al. 1976; Singh et al. 1981). Studies with pure mineral phases demonstrate that hydrous oxides of Fe and Al and amorphous aluminosilicates have a high affinity for Se(IV,VI) (Leckie et al. 1980; Hingston et al. 1968b; Hingston et al. 1974; Rajan 1979; Rajan and Watkinson 1976) which significantly exceeds that of layer lattice silicates (Frost and Griffin 1977a; Hamdy and Gissel-Nelson 1977). Though selenite ($\text{pK}_2:7.9$) and selenate ($\text{pK}_2:1.7$) differ appreciably in their acidity, little difference is seen in their adsorption by soil (Singh et al. 1981). Selenate may be adsorbed more strongly by clay minerals than selenite (Frost and Griffin 1977) while the inverse holds for hydrous oxides of Fe (Leckie et al. 1980; Benjamin and Bloom 1981).

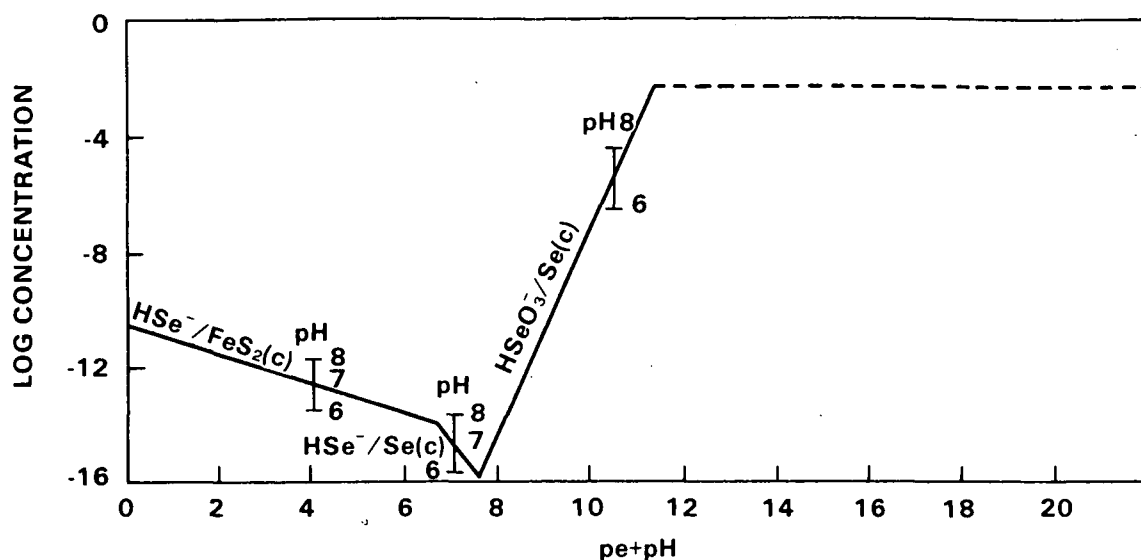


Figure 19-4. The effect of redox potential ($pe + pH$) on the solubility of $FeSe_2(c)$ and $Se(c)$.

The adsorption of $Se(IV)$ and $Se(VI)$ on goethite, amorphous iron oxyhydroxide, and gibbsite is strongly pH dependent (Table 19-1) (Hingston et al. 1968; Leckie et al. 1980; Hingston et al. 1972). These anions are strongly adsorbed under acidic conditions, but fractional adsorption decreases with increasing pH. Decreasing adsorption occurs in a pH region characteristic of each anion. The adsorption of $Se(IV)$ and $Se(VI)$ are controlled by and influence the surface charge on the adsorbent. Limited experimental evidence suggest that, at a given pH, Se adsorbs to neutral and positively charged amphoteric oxide surfaces displacing water, hydroxyls and other adsorbed ligands (e.g., sulfate, silicate) until the surface is neutral in charge (Rajan 1979; Rajan and Watkinson 1976).

The presence of competing anions (Table 19-1) may reduce $Se(IV)$ and $Se(VI)$ adsorption by utilization of limited ligand exchange sites and reduction in surface net positive charge. Phosphate reduces Se adsorption on goethite, though some sites are specific to Se (Hingston et al. 1971). Sulfate reduces SeO_4^{2-} adsorption on amorphous iron oxyhydroxide in a manner consistent with the competitive Langmuir equation (Leckie et al. 1980). Selenite adsorption on amorphous Fe oxyhydroxide in the presence of fly ash leachate containing SO_4^{2-} , Ca^{2+} , K^+ , and Na^+ differs appreciably from adsorption in inert electrolyte (Leckie et al. 1980). Selenite adsorption in fly ash leachate below pH 10 is reduced by competition with SO_4^{2-} , but is increased above pH 10 by the apparent adsorption of aqueous Se complexes.

Selenium adsorption on oxides and soils conforms to the Langmuir equation, though a multi-site Langmuir equation is needed on some soils (Hingston et al. 1968; Singh 1982). The Langmuir constants on oxides vary significantly with pH (Hingston et al. 1968). The pH-dependent adsorption of Se on hydrous oxides and the resulting effects on net surface charge have been modeled by several investigators (Bowden et al. 1980; Davis and Leckie 1980). Reactions leading to the formation of the surface species $\text{SOH}_2\text{SeO}_3^-$, $\text{SOH}_2\text{SeO}_3\text{H}$, $\text{SOH}_2\text{SeO}_4^-$ and $\text{SOH}_2\text{SeO}_4\text{N}$ were needed to adequately describe the pH-dependent adsorption of Se(IV) and Se(VI) on amorphous iron oxyhydroxide (Leckie et al. 1980; Davis and Leckie 1980; Benjamin and Bloom 1981). Equilibrium constants for these reactions were valid over a range of sorbate concentration and ionic strength.

Selenium exhibits variable desorbability from oxide surfaces and soils. Selenite adsorption is irreversible on goethite (Hingston et al. 1974) partially reversible on hydrous alumina (Rajan 1979), and reversible on gibbsite (Hingston et al. 1974). The adsorption of selenite on $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{am})$ is reversible in response to pH change (Leckie et al. 1980). Desorption is accompanied by OH^- adsorption and a decrease in solution pH (Hingston et al. 1974; Rajan 1979). Sulfate and PO_4^{2-} are effective in releasing up to 90% of soil adsorbed SeO_3^{2-} and SeO_4^{2-} (Singh et al. 1982).

Table 19-1. ADSORPTION CONSTANTS FOR SELENIUM

Adsorbent		Adsorbate		Electrolyte			Adsorption Measurements		References
Identity	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants ^(a)	Value ^(b)	
Amorphous Iron oxyhydroxide [Fe ₂ O ₃ ·H ₂ O (am)]	---	182	10 ⁻³ -10 ⁻⁷ Se(VI)	NaNO ₃	0.1	3-11	K ^{Int} _{SeO₄}	4.8	Davis and Leckie 1980
							K ^{Int} _{HSeO₄}	9.1	
Amorphous Iron oxyhydroxide [Fe ₂ O ₃ ·H ₂ O (am)]	---	182	10 ⁻³ Se(VI)	NaNO ₃	0.1	3-11	K ^{Int} _{SeO₄}	9.90	Benjamin and Bloom 1981
							K ^{Int} _{HSeO₄}	12.2	
			10 ⁻⁴ Se(VI)	NaNO ₃	0.1	3-11	K ^{Int} _{SeO₄}	6.65	
							K ^{Int} _{HSeO₄}	8.80	
Amorphous Iron oxyhydroxide [Fe ₂ O ₃ ·H ₂ O (am)]	---	182	10 ⁻³ Se(IV)	NaNO ₃	0.1	3-11	K ^{Int} _{SeO₃}	7.80	Benjamin and Bloom 1981
							K ^{Int} _{HSeO₃}	9.90	
			10 ⁻⁴ Se(IV)	NaNO ₃	0.1		K ^{Int} _{SeO₃}	7.70	
							K ^{Int} _{HSeO₃}	7.75	
Goethite	---	32	10 ⁻³ - 10 ⁻⁵ Se(IV)	NaCl	0.01-1.0	3-11	A _m K _L	20-120 3.5-5.0	Hingston et al. 1968
Kaolinite	15.1	34.2	10 ⁻³ - 10 ⁻⁴ Se(IV)	landfill leachate	---	3	A _m , K _L	4.20, 3.23	Frost, and Griffin 1977
						5		2.93, 3.37	
						7		2.40, 3.26	
Montmorillonite	79.5	86.2	10 ⁻³ - 10 ⁻⁴ Se(IV)	landfill leachate	---	3	A _m , K _L	8.34, 3.43	
						5		6.99, 3.49	
						7		5.23, 3.25	

Table 19-1 (Contd). ADSORPTION CONSTANTS FOR SELENIUM

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		References
Identity	CEC meq/100g	S _p A _s m ² /g	Conc., M	Identity	Conc., M	pH	Constants (a)	Value	
Allophane	---	168	10 ⁻⁴ - 10 ⁻²	KCl	0.1	5.0	A _m ^I , K _L ^I	110, 4.12	Rajan and Watkinson 1976
			Se(IV)				A _m ^{II} , K _L ^{II}	179, 2.54	
<u>Soils</u>									
0.42% Org C, 17.8% clay 2.6% free Fe	13.75	---	10 ⁻⁴ - 10 ⁻²	NaCl	Variable	7.6	Se(IV) A _m ^I , K _L ^I A _m ^{II} , K _L ^{II}	8.5, 3.34 87, 1.52	Singh et al. 1981
			Se(IV), Se(VI)				Se(VI) A _m ^I , K _L ^I A _m ^{II} , K _L ^{II}	13, 3.39 94, 1.89	
0.42% Org C, 17.6% clay, 2.2% free Fe, 2.8% CaCO ₃	12.3	---	10 ⁻⁴ - 10 ⁻²	NaCl	Variable	8.1	Se(IV) A _m ^I , K _L ^I A _m ^{II} , K _L ^{II}	18, 2.96 85, 1.79	
			Se(IV), Se(VI)				Se(VI) A _m ^I , K _L ^I A _m ^{II} , K _L ^{II}	16, 3.46 128, 1.88	
0.92% Org C, 18.4% clay, 2.1% free Fe	16.0	---	10 ⁻⁴ - 10 ⁻²	NaCl	Variable	7.8	Se(IV) A _m ^I , K _L ^I A _m ^{II} , K _L ^{II}	16.5, 3.59 51.5, 2.24	
			Se(IV), Se(VI)				Se(VI) A _m ^I , K _L ^I A _m ^{II} , K _L ^{II}	3.5, 4.27 25.5, 3.53	
0.42% Org C, 8.8% clay, 2.8% free Fe	10.4	---	10 ⁻⁴ - 10 ⁻²	NaCl	Variable	7.8	Se(IV) A _m ^I , K _L ^I A _m ^{II} , K _L ^{II}	2.5, 2.00 240, 1.23	
			Se(IV), Se(VI)				Se(VI) A _m ^I , K _L ^I A _m ^{II} , K _L ^{II}	30, 252 128, 1.73	
0.32% Org C, 9.6% clay, 2.4% free Fe	10.0	---	10 ⁻⁴ - 10 ⁻²	NaCl	Variable	10.1	Se(IV) A _m ^I , K _L ^I A _m ^{II} , K _L ^{II}	10, 2.91 79.5, 7.08	
			Se(IV), Se(VI)				Se(VI) A _m ^I , K _L ^I A _m ^{II} , K _L ^{II}	100, 1.94	

(a) K^{Int} = intrinsic adsorption constants of ionic species, log K_L = Langmuir constant, log M⁻¹ A_m = Langmuir adsorption maximum, $\mu\text{mol g}^{-1}$ $A_m^I, K_L^I, A_m^{II}, K_L^{II}$ = two adsorption sites

(b) () = estimated values

Section 20

SODIUM

Sodium (Na) is a soluble constituent in most subsurface environments. Except at higher pH where carbonate complexes become important, Na is found in solution primarily as the univalent ion, Na^+ . The attenuation of Na in soil and subsoil is controlled primarily by ion exchange reactions. Solubility reactions, e.g., precipitation, is rarely of consequence except in evaporite environments. Though subsurface mobility of Na is high, the common problem of soil sodicity in low rainfall areas indicates that when present in soil solution in high concentration, Na may be retained by and dominate soil cation exchange sites.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIES

Sodium exhibits only +1 valence state. Sodium is an important constituent of zeolites (e.g., analcime) and feldspathic igneous aluminosilicate minerals such as albite. However, the geochemical conditions required for their formation are rarely encountered in soils (Lindsay 1979).

To determine the relative abundance of Na^+ species in ground waters representative of leachates, activities of different Na species (when $\text{Na}^+ = 10^{-3} \text{ M}$) were plotted (Figure 20-1) using the thermodynamic data (Ball et al. 1980) contained in the geochemical model MINTEQ (Felmy et al. 1983) and the formation constants for NaNO_3^0 and NaOH^0 reported by Smith and Martell (1976). Under the assumed conditions (Figure 20-1) Na^+ is the only important species up to pH values of about 10. At higher pH values, carbonate complexes of Na become dominant.

PRECIPITATION/DISSOLUTION

Most Na minerals are very soluble and hence do not form in well-drained humid conditions. Sodium concentrations are thus primarily controlled by adsorption/desorption reactions rather than precipitation/dissolution.

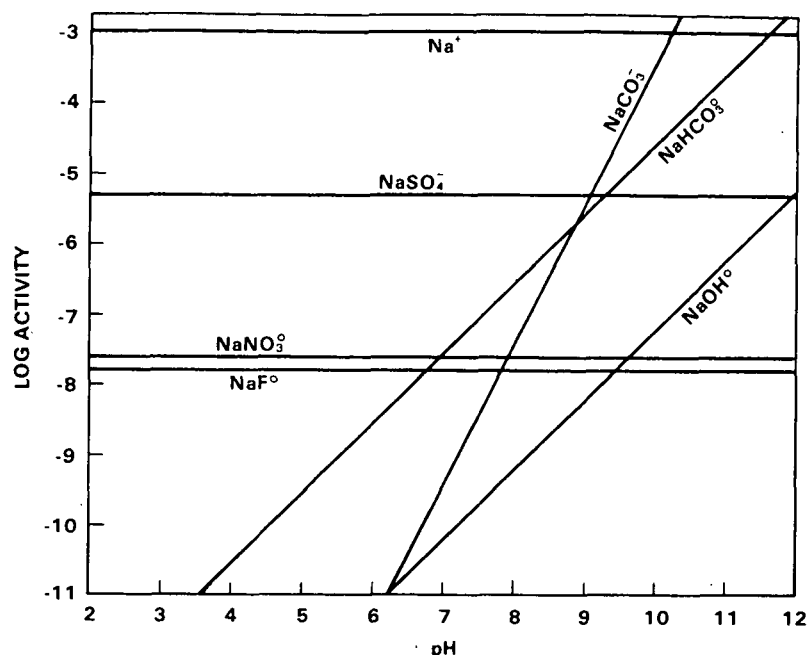


Figure 20-1. Activities of different Na species when activity of $\text{Na}^+ = \text{SO}_4^{2-} = 10^{-3}$, $\text{NO}_3^- = 10^{-4}$, and CO_2 (gas) = $10^{-3.52}$ atmospheres.

ADSORPTION/DESORPTION

The adsorption of Na by soils occurs primarily by ion exchange (e.g., Sheta et al. 1981). This process is electrostatic and Na is only weakly bound to amphoteric hydrous Mn in Fe oxides below their isoelectric points (Davis 1978; Davis et al. 1978; Davis and Leckie 1980; Balistrieri and Murray 1981; Loganathan and Burau 1973). Sodium is held weakly by cation exchange materials because of its univalent charge and large hydrated radius (Gaines and Thomas 1953). The preference of soil clays for monovalent cations follows the lyotropic series $\text{Li}^+ < \text{Na}^+ < \text{H}_3\text{O}^+ < \text{K}^+ < \text{NH}_4^+ < \text{Pb}^+ < \text{Cs}^+$ reflecting increasing ionic radius, decreasing polarizing power and ionic hydration from left to right in the series (Talibudeen 1981). Adsorption of Na by soil is governed by mass action on cation exchange sites. Thus, Na retention is controlled by the concentrations of cations (e.g., Ca, Mg, K) in solution and the nature and selectivity of cation exchange constituents.

Sodium exchange equilibria with various cationic constituents have been evaluated on soils and layer lattice silicates (Table 20-1). Sodium-calcium exchange in soil has received considerable research attention because of its importance in soil sodicity (Yadav and Girdhar 1981; Kelley 1962; Mondal 1973). Soil sodicity occurs by gradual replacement of exchangeable Ca by Na. The variability of the Na/Ca selectivity

coefficient is small among different soil types (Sheta et al. 1981; Levy and Feigenbaum 1977). An increase in exchangeable sodium percentage (ESP) is encouraged as the ratio of Mg/Ca increases in soil solution. Magnesium is more weakly bound to cation exchange sites than Ca, and Na is more readily adsorbed by Mg-saturated than Ca-saturated soil (Mondal 1973). The ESP in calcareous soils, however, is less sensitive to the Mg/Ca ratio than noncalcareous soil (Yadav and Girdhar 1981). On clay minerals, heterovalent exchange reactions between Na^+ and trace metal cations exhibit ideal thermodynamic behavior, are reversible and may be characterized by the Vanselow selectivity coefficient (Maes et al. 1976; Sposito and Mattigod 1979; Sposito et al. 1981). Certain anions, including Cl^- , I^- , Br^- , and SO_4^{2-} in increasing concentration up to ionic strength 1 decrease Na adsorption on bentonite, while increasing pH; bicarbonate concentrations increase retention (Sommerfeldt and Peterson 1963). Though Na is weakly bound to most cation exchange sites in soil, the presence of Na selective layer lattice silicates (paragonite) and zeolites (El-Nahal and Whittig 1973; Schulz et al. 1964) suggest that in isolated instances Na may be strongly retained by certain mineral constituents.

Table 20-1. ADSORPTION CONSTANTS FOR SODIUM

Adsorbent			Adsorbate		Electrolyte		Adsorption Measurement		References
Identity ^(a)	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants ^(b)	Value	
Clay Minerals									
Bentonite, Na-saturated	92	-	-	NaBa	1.0	7.4	A	660	Sommerfeldt and Peterson 1963
				NaI	1.0	7.5	A	680	
				NaCl	1.0	7.1	A	760	
				Na ₂ SO ₄	0.5	7.6	A	770	
				NaHCO ₃	1.0	8.2	A	940	
				NaOH	1.0	12.3	A	1150	
Bentonite	103	-	-	Seawater	35%	-	A	623	Neal 1977
				Seawater	25	-	A	646	
				Seawater	15	-	A	554	
				Sawater	5	-	A	521	
Soil	% Clay	% O.M.					Soil		Yadav and Girdhar 1981
Sandy loam	20.0	1.06	10.00	-	-	-	7.95		
Untreated soil				Sol. A	Na ⁺ Mg ²⁺ Ca ²⁺	0.04 ~0.015 ~0.003	A	14.5-15.7	
				Sol. B	Na ⁺ Mg ²⁺ Ca ²⁺	0.06 ~0.002 ~0.0005	A	28.1-32.0	
				Sol. C	Na ⁺ Mg ²⁺ Ca ²⁺	0.08 ~0.002 ~0.0005	A	47.6-55.5	
CaCO ₃ removed	-	-	-	Sol. A			A	16.0-17.9	
				Sol. B			A	32.0-38.2	
				Sol. C			A	55.0-67.5	
11 Egyptian Soils	11.9-47.5	-	-	-	-	-	K ^C _{NA}	47±7	Sheta Et Al. 1981
Clay	% Clay	% O.M.							Levy and Feigenbaum 197.
	55.0	1.8	42.4	-	ΣCl ⁻	0.05	A	82	
					ΣCl ⁻	0.05	A	151	
					ΣCl ⁻	0.05	A	158	

Table 20-1 (Contd). ADSORPTION CONSTANTS FOR SODIUM

Adsorbent					Adsorbate	Electrolyte			Adsorption Measurement		References
Identity ^(a)			CEC meq/100g	S _A m ² /g	Conc., M	Identity	Conc., M	pH	Constants ^(b)	Value	
Soil Clay	%Clay 58.0	% O.M. 0.5	32.2	-	0.025	ΣCl ⁻	0.05	-	A	22	
					0.04	ΣCl ⁻	0.05		A	34	
					0.05	ΣCl ⁻	0.05		A	59	
Clay	74.5	3.4	43.0	-	0.025	ΣCl ⁻	0.05	-	A	24	
					0.04	ΣCl ⁻	0.05		A	32	
					0.05	ΣCl ⁻	0.05		A	70	
Loess	16.2	0.5	13.4	-	0.025	ΣCl ⁻	0.05	-	A	5	
					0.04	ΣCl ⁻	0.05		A	10	
					0.05	ΣCl ⁻	0.05		A	19	
Calcareous	31.1	1.6	26.2	-	0.025	ΣCl ⁻	0.05	-	A	24	
					0.04	ΣCl ⁻	0.05		A	27	
					0.05	ΣCl ⁻	0.05		A	40	

(a) O.M. = organic matter

(b) A = adsorption, $\mu\text{mol g}^{-1}$ K_{Na} = exchange coefficient $K_{\text{NAT}}^{\text{INT}}$ = log Intrinsic Adsorption Constant

Goethite	-	51.8	0.1-0.7	-	-	5.10	$K_{\text{Na}^+}^{\text{INT}}$	(1.12)	Balistreria and Murray 1981
Fe ₂ O ₃ ·H ₂ O (AM)	-	600	-	-	-	-	$K_{\text{Na}^+}^{\text{INT}}$	(1.7)	Davis and Lecki 1980
Fe(OH) ₃	-	600	-	-	-	-	$K_{\text{Na}^+}^{\text{INT}}$	1.7	Davis 1977
γ-Al ₂ O ₃	-	117	-	-	-	-	$K_{\text{Na}^+}^{\text{INT}}$	2.3	Davis, et al. 1978

Section 21

SULFATE

Sulfate, a common anion in soil and subsurface environments, may under natural conditions exceed concentrations of 10^{-2} M in soil solutions or pore waters. Although aqueous complexes with Al (AlSO_4^+) are important at low pH (<4), the SO_4^{2-} ion predominates at $\text{pe} + \text{pH} > 4$. Most naturally occurring solids of sulfate are quite soluble; however, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) under poorly drained arid soils and aluminum sulfates such as basaluminite and alunite at low pH values may become important solubility-controlling solids. With the exception of highly weathered and volcanic-ash-derived soils, sulfate is weakly adsorbed by soil. Hydrous oxides of Al and Fe are the most important adsorbents. Adsorption is pH dependent and greatest at a low pH. A number of anions present in utility waste leachate (e.g., SeO_4^{2-} , AsO_4^{3-}) will compete with SO_4^{2-} for specific adsorption sites in soil and substrata.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIES

Sulfur ranges in oxidation states from +6 to -2. Except for very reducing conditions ($\text{pe} + \text{pH} < 4$), SO_4^{2-} is the stable aqueous species (Lindsay 1979). Most of the known solid compounds of SO_4^{2-} are very soluble. Because sulfate is a major anion, only the sulfate compounds with major cations can be solubility-controlling solids. One such compound (gypsum) has been identified in some arid soils and sedimentary deposits.

To determine the relative abundance of SO_4^{2-} species in ground waters representative of leachates, activities of different SO_4^{2-} species (when $\text{SO}_4^{2-} = 10^{-3}$ M) were plotted (Figure 21-1) using the thermodynamic data (Ball et al. 1980) contained in the geochemical model MINTEQ (Felmy et al. 1983). Under the assumed conditions (Figure 21-1), SO_4^{2-} is the dominant species at pH values >4 ; except for about 6% contribution of CaSO_4^0 to total soluble sulfur, all of the other species (such as MgSO_4^0 , NaSO_4^- , FeSO_4^+ , AlSO_4^+ , PbSO_4^0 , CdSO_4^0) do not contribute significantly. Under the assumed conditions AlSO_4^+ will be the dominant species at pH values ≤ 4 .

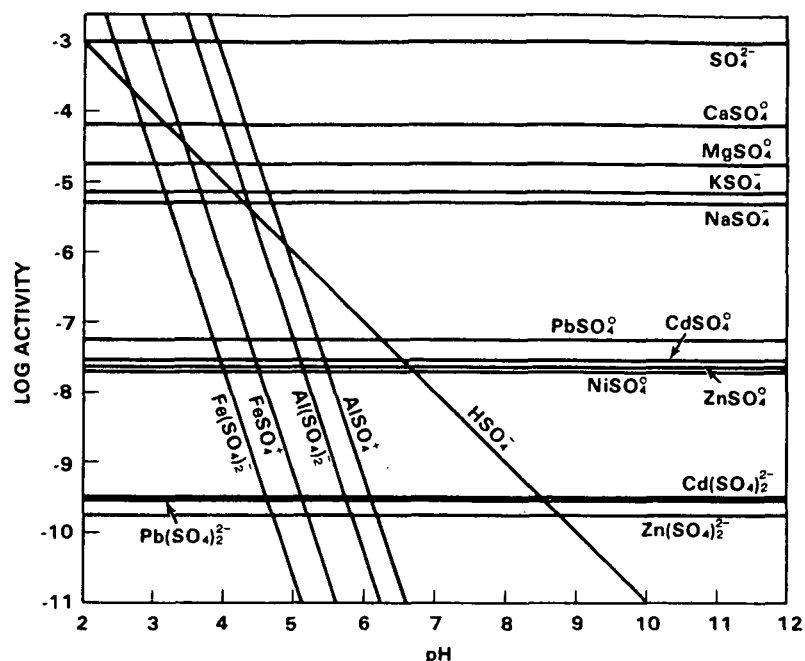


Figure 21-1. Activities of different sulfate species when activity of SO_4^{2-} , $\text{Na}^+ = \text{Ca}^{2+} = \text{K}^+ = 10^{-3}$, $\text{Mg}^{2+} = 10^{-4}$, $\text{Al}^{3+} = \text{Fe}^{3+} = \text{Pb}^{2+} = \text{Ni}^{2+} = \text{Cd}^{2+} = 10^{-7}$, and $\text{CO}_2(\text{gas}) = 10^{-3.52}$.

PRECIPITATION/DISSOLUTION

The major attenuation mechanism for sulfate is adsorption/desorption. Only in limited environments, will sulfate solubility-controlling solids form. Under oxidizing and alkaline conditions, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) has been identified in some poorly drained arid soils and sedimentary deposits (Harward and Reisenauer 1966, Reitemeir 1946). Under acidic conditions Al^{3+} and Fe^{3+} become major cations and where SO_4^{2-} is present or can form in large quantities such as basaluminite due to pyrite oxidation $[\text{Al}_4(\text{OH})_{10}\text{SO}_4 \cdot 5\text{H}_2\text{O}]$, AlOHSO_4 , alunite $[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]$, $\text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ jarosite $[\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2]$, and natrojarosite $[\text{NaFe}_3(\text{OH})_6(\text{SO}_4)_2]$ have been identified and are potential solubility controlling phases (Adams and Ramajfi 1977; Singh and Brydon 1969; Van Breemen and Harmsen 1975; Doner and Lynn 1977). Under low redox potentials SO_4^{2-} is reduced to S^{2-} and the latter species is primarily attenuated through precipitation mechanism.

ADSORPTION/DESORPTION

Sulfate is an important and ubiquitous anion in soil. In many soils SO_4^{2-} is the prominent anionic constituent in soil solution, especially in gypsiferous semiarid

and arid sulfate soils. Much of the available literature on SO_4^{2-} retention has evaluated adsorption/desorption reactions as a controlling factor in plant nutrition. In general, sulfate is weakly retained by soils (Table 21-1). Soils differ markedly in their adsorption capacity (Chao et al. 1962a, 1962b; Hasan et al. 1970); highly weathered and volcanic-ash-derived soils may adsorb significant quantities of SO_4^{2-} . Most sulfate adsorption in soil is associated with hydrated Al and Fe oxides (Harward and Reisenauer 1966; Chao et al. 1962a; Couto et al. 1979; Chao et al. 1964; Aylmore et al. 1967) or amorphous aluminosilicates (Hasan et al. 1970; Rajan 1979; Gebhardt and Coleman 1974). Experimental evidence suggests that SO_4^{2-} retention occurs by specific adsorption on soils (Couto et al. 1979), allophanic clays (Rajan 1978a), amorphous iron oxyhydroxide (Davis and Leckie 1980), and gibbsite (Hingston et al. 1974). Other investigators note, however, that SO_4^{2-} adsorption does not decrease the pzc of soil (Arnold 1977) or goethite (Yates and Healy 1975) implying that specific adsorption does not occur and SO_4^{2-} does not reach the inner Helmholtz plane.

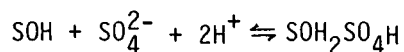
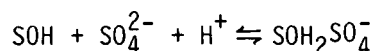
Sulfate adsorption exhibits marked dependency on the pH of soils (Couto et al. 1979; Gebhardt and Coleman 1974), layer lattice silicates (Chao et al. 1962c; Aylmore et al. 1967), amorphous iron oxyhydroxide (Davis and Leckie 1979), goethite (Balistrieri and Murray 1981), hydrous alumina (Rajan 1978), and allophane (Rajan 1979), with greater adsorption occurring at low pH levels. This arises primarily from the development of pH-dependent positive charge on the surfaces of hydrous iron and/or aluminum oxide or on the crystal edges of clay minerals (especially kaolinite) at low pH values (Chao et al. 1962c; Parfitt and Smart 1978; Rajan 1978b). Additionally, the proportion of HSO_4^- increases with reduced pH; HSO_4^- is more favorably adsorbed by hydroxylated surfaces (Davis and Leckie 1980; Hingston et al. 1972).

Competing inorganic and organic ligands have variable effects on SO_4^{2-} adsorption by soil and model adsorbents. The presence of chloride, nitrate, acetate, borate, silicate, or arsenite have little or no effect on SO_4^{2-} adsorption by soil (Chao 1964). In contrast, soil adsorption of SO_4^{2-} is significantly reduced by selenate, selenite, arsenate, molybdate, fluoride, thiocyanate, and phosphate (Chao 1964). Sulfate and SeO_4^{2-} compete effectively for adsorption sites on amorphous iron oxyhydroxide (Leckie et al. 1980). Organic ligands commonly present in soil such as oxalate, tartrate, malate, and gluconate also suppress SO_4^{2-} adsorption (Chao 1964). Inorganic and organic ligands may reduce SO_4^{2-} adsorption by competing for available adsorption sites, by formation of stable surface chelates on Fe and Al oxide surfaces, or by precipitation as a new surface solid phase.

The effect of electrolyte concentration on SO_4^{2-} adsorption is a pH-dependent phenomenon related to the zero point of charge of the soil. Increasing electrolyte concentration decreases the interfacial potential at the solid/solution interface, which decreases SO_4^{2-} adsorption at a pH less than the zero point of charge (pH_{zpc}) and increases adsorption above the pH_{zpc} (Mekaru and Vehara 1972).

Although formation of insoluble basic Al and Fe sulfates is implicated as a retention mechanism of SO_4^{2-} in soil (Singh and Brydon 1969; Adams and Ramajfih 1977), the specific adsorption of SO_4^{2-} by soil is attributed to ligand exchange with displacement of surface hydroxyl or aquo groups. Strong evidence is presented suggesting that monodentate complexes are formed with HSO_4^- as the primary adsorbing species (Aylmore et al. 1967; Gebhardt and Coleman 1974), though arguments are made supporting the formation of bidentate SO_4^{2-} surface complexes (Rajan 1978a; Rajan 1978b; Parfitt and Russel 1977).

In contrast to ligand exchange, excellent simulation of SO_4^{2-} desorption on amorphous iron oxyhydroxide and goethite is obtained using an adsorption model based on surface complexation reactions (noted below) with protonated surface groups (Davis and Leckie 1980; Balistrieri and Murray 1982).



Surface complexation reactions describe the observed increase in pH accompanying adsorption as due to proton consumption at the plane of adsorption rather than ligand displacement.

Adsorbed sulfate exhibits variable desorbability from soil and model adsorbents. Sulfate adsorption exhibits partial to full reversibility in soils (Sanders and Tinker 1975; Chao et al. 1962a; Couto et al. 1979; Gebhardt and Coleman 1974). Some mineral soils (B horizons) high in hydrated Fe oxides or amorphous aluminosilicates exhibit poor desorption of adsorbed SO_4^{2-} (Gebhardt and Coleman 1974; Couto et al. 1979). Adsorption of SO_4 is irreversible on hematite ($\alpha\text{-Fe}_2\text{O}_3$) and pseudoboehmite ($\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) (Aylmore et al. 1967; Sanders and Tinker 1975), but reversible on kaolinite (Aylmore et al. 1967). Thus, the desorption of specifically adsorbed SO_4^{2-} in soil will depend strongly on the mineralogic characteristics of the adsorbents.

Table 21-1. ADSORPTION CONSTANTS FOR SULFATE

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		References	
Identity ^(a)	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants ^(b)	Value ^(c)		
Clay Minerals										
Allophane synthetic	-	278	0 - 10 ^{-2.3}	NaCl	0.01	5.0	A _m , K _L	(33, 3.2)	Rajan 1979a	
	-	420	-	-	-	-	-	(130, 3.5)		
Kaolinite API-9	-	17.7	10 ^{-3.3} - 10 ^{-1.3}	-	-	4.6	A _m ^I , K _L ^I	(2.8, 6.4, 2.4, 4.4)	Aylmore et al. 1967	
Australian	-	16.9	-	-	-	-	A _m ^{II} , K _L ^{II}	(4.6, 6.1, 5.6, 3.9)		
Alumina										
γ-Al ₂ O ₃ ·H ₂ O	-	165.5	10 ^{-3.3} - 0.05	-	-	4.6	A _m , K _L	(450, 5.8)	Aylmore et al. 1967	
γ-Al ₂ O ₃ ·3H ₂ O	-	58	10 ^{-5.8}	-	-	5.0	A	(50)	Hingston et al. 1972	
Hydrous alumina	-	230	-	NaCl	0.01	5.0	A _m	408	Rajan 1979b	
		197	-	NaCl	0.01	5.0	A _m , K _L	(400, 4.9)	Rajan 1978	
Al-oxide coated soil										
Willamette Chehalis										
Al ₂ O ₃ %										
0	0	-	-	10 ^{-2.6}	-	-	5.0	A	(1.3 0.3)	Chas et al. 1964
2.7	2.6	-	-	10 ^{-2.6}	-	-	5.0	A	(4.3 3.8)	
4.0	4.0	-	-	10 ^{-2.6}	-	-	5.0	A	(9.5 7.5)	
5.0	5.1	-	-	10 ^{-2.6}	-	-	5.0	A	(13.3 11.7)	
6.2	6.2	-	-	10 ^{-2.6}	-	-	5.0	A	(14.7 14.2)	
Fe Oxides										
Goethite, γ-FeOOH		81	10 ^{-2.8} - 10 ^{-2.5}	-	-	5.0	A	(72)	Hingston et al. 1972	
Hematite, α-Fe ₂ O ₃		26.7	10 ^{-3.3} - 0.05	-	-	4.6	A _m , K _L	(70, 6.1)	Aylmore et al. 1967	
Amorphous Fe oxide		182	10 ⁻⁵ - 10 ⁻³	NaNO ₃	0.1	5.0	A _m , K _L	(1160, 4.5)	Davis and Leckie 1978	

Table 21-1 (Contd). ADSORPTION CONSTANTS FOR SULFATE.

Adsorbent				Adsorbate		Electrolyte			Adsorption Measurements		References
Identity (a)		CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)		
Fe-oxide coated soil											
Willamette											
Chehalis											
% Fe ₂ O ₃											
0	0	-	-	10 ^{-2.6}	-	-	5.0	A	(1.3 0.3)	Chas et al. 1964	
-	1.9	-	-	10 ^{-2.6}	-	-	5.0	A	(- 0)		
2.4	2.5	-	-	10 ^{-2.6}	-	-	5.0	A	(0 0)		
2.9	2.7	-	-	10 ^{-2.6}	-	-	5.0	A	(0.7 0.4)		
3.4	3.2	-	-	10 ^{-2.6}	-	-	5.0	A	(1.3 0.8)		
3.7	3.8	-	-	10 ^{-2.6}	-	-	5.0	A	(2.0 2.2)		
4.9	-	-	-	10 ^{-2.6}	-	-	5.0	A	(3.5 -)		
Goethite, α-FeOOH		-	51.8	10 ^{-3.4}	NaCl	0.01	5.0	A	(29.4)	Balistrieri and Murray 1981	
		-	51.8	10 ^{-3.7}	NaCl	10 ⁻³	5.0	A	(3.1)		
		-	-	-	Seawater	~0.7	8.0	*K ^{int} _{SO₄}	-9.1, -14.4		
								*K ^{int} _{HSO₄}			
								K ^{int} _{SO₄}	(3.5, 6.8)		
								K ^{int} _{HSO₄}			
Amorphous Fe ₂ O ₃ ·H ₂ O		-	60	-	NaNO ₃	0.1	-	*K ^{int} _{SO₄}	-9.9, -15.9	Davis and Leckie 1982	
								*K ^{int} _{HSO₄}			
								K ^{int} _{SO₄}	4.8, 8.7		
								K ^{int} _{HSO₄}			
Soils	Depth, cm	% Fe	% O.M.								
Fullerton								Soil			
0-30	1.06	1.75	4.9	-	10 ^{-2.7}	-	-	4.2	A	3.1	Johnson and Henderson 1979
30-60	1.46	0.65	2.1	-	10 ^{-2.7}	-	-	4.4	A	1.3	
60-80	1.24	0.62	2.7	-	10 ^{-2.7}	-	-	4.2	A	0.9	
80-120	2.38	0.63	5.4	-	10 ^{-2.7}	-	-	4.2	A	2.7	
120-200	2.74	0.62	8.9	-	10 ^{-2.7}	-	-	4.2	A	1.6	
Free Fe, %		Free Al, %						Soil			
Robertson	5.2	1.2	16.1	-	10 ^{-4.1} - 10 ^{-2.8}	-	-	4.2	A _m , K _L	(11.2, 2.9)	Barrow 1972
					10 ^{-4.1} - 10 ^{-2.8}	CaCl ₂	0.002	4.2	A _m , K _L	(10.5, 3.4)	
					10 ^{-4.1} - 10 ^{-2.8}	CaCl ₂	0.005	4.2	A _m , K _L	(11.1, 3.6)	
					10 ^{-4.1} - 10 ^{-2.8}	CaCl ₂	0.01	4.2	A _m , K _L	(11.6, 3.6)	
					10 ^{-4.1} - 10 ^{-2.8}	CaCl ₂	0.02	4.2	A _m , K _L	(11.5, 3.7)	

Table 21-1 (Contd). ADSORPTION CONSTANTS FOR SULFATE

Adsorbent					Adsorbate		Electrolyte			Adsorption Measurements		References
Identity (a)			CEC	S ₂ A.	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)		
Soil	Free Fe, 9b	Free Al, 9b	meq/100g	m ² /g								
Wungong	0.8	0.3	10.3	-	10 ^{-4.1} - 10 ^{-2.8} 10 ^{-4.1} - 10 ^{-2.8} 10 ^{-4.1} - 10 ^{-2.8} 10 ^{-4.1} - 10 ^{-2.8} 10 ^{-4.1} - 10 ^{-2.8}	- CaCl ₂ CaCl ₂ CaCl ₂ CaCl ₂	- 0.002 0.005 0.01 0.02	5.2 5.2 5.2 5.2 5.2	A _m , K _L A _m , K _L A _m , K _L A _m , K _L A _m , K _L	(1.2, 3.3) (2.8, 3.4) (3.2, 3.4) (3.2, 3.5) (3.1, 3.6)	Barrow 1972	
Manjimup	2.1	0.5	26.3	-	10 ^{-4.1} - 10 ^{-2.8} 10 ^{-4.1} - 10 ^{-2.8} 10 ^{-4.1} - 10 ^{-2.8} 10 ^{-4.1} - 10 ^{-2.8} 10 ^{-4.1} - 10 ^{-2.8}	- CaCl ₂ CaCl ₂ CaCl ₂ CaCl ₂	- 0.002 0.005 0.01 0.02	6.2 6.2 6.2 6.2 6.2	A _m , K _L A _m , K _L A _m , K _L A _m , K _L A _m , K _L	(2.6, 3.4) (3.6, 3.5) (4.4, 3.5) (4.6, 3.5) (4.7, 3.5)		
Soil	untreated + 6.5 μmol g ⁻¹ P + 19.4 μmol g ⁻¹ P + 32.3 μmol g ⁻¹ P		-	-	10 ^{-3.7} - 10 ^{-2.6} 10 ^{-3.7} - 10 ^{-2.6} 10 ^{-3.7} - 10 ^{-2.6} 10 ^{-3.7} - 10 ^{-2.6}	CaCl ₂ CaCl ₂ CaCl ₂ CaCl ₂	0.01 0.01 0.01 0.01	- - - -	A _m , K _L A _m , K _L A _m , K _L A _m , K _L	(9.7, 3.2) (8.0, 3.2) (7.1, 3.1) (6.0, 2.9)	Barrow 1969	
	Fe ₂ O ₃ , %	Al ₂ O ₃ , %	O.M., %						Soil			
Aiken	6.84	5.20	6.8	-	10 ^{-3.8} - 10 ^{-2.5}	-	-	5.5	A _m , K _L	(4.1, 3.2)	Chas et al. 1962a, b	
Knappa	5.23	4.70	18.3	-	10 ^{-3.8} - 10 ^{-2.5}	-	-	6.2	A _m , K _L	(2.7, 3.5)		
Astoria	4.35	3.68	12.8	-	10 ^{-3.8} - 10 ^{-2.5}	-	-	5.3	A _m , K _L	(3.6, 3.7)		
Quillayute	4.50	8.69	17.6	-	10 ^{-3.8} - 10 ^{-2.5}	-	-	5.5	A _m , K _L	(3.3, 3.9)		
Aiken			-	-	>10 ^{-2.5}	-	-	-	K _F , 1/N	0.124, 0.483	Chas 1962a	
Knappa			-	-	>10 ^{-2.5}	-	-	-	K _F , 1/N	0.0745, 0.538		
Astoria			-	-	>10 ^{-2.5}	-	-	-	K _F , 1/N	0.127, 0.516		
Quillayute			-	-	>10 ^{-2.5}	-	-	-	K _F , 1/N	0.0955, 0.576		
Quillayute (untreated)			-	-	10 ^{-3.8} - 10 ^{-2.5}	-	-	-	K _F , 1/N	(0.070, 0.70)	Chas et al. 1962c	
1) H ₂ O ₂ treated (O.M. & MnO ₂ removed)			-	-	10 ^{-3.8} - 10 ^{-2.5}	-	-	-	K _F , 1/N	(0.024-0.035, 0.72-0.77)		
2) 1+Dithionite, etc. (Fe removal)			-	-	10 ^{-3.8} - 10 ^{-2.5}	-	-	-	K _F , 1/N	(0.008, 0.66)		
3) 1+0.5 M NaOH (Al removal)			-	-	10 ^{-3.8} - 10 ^{-2.5}	-	-	-	K _F , 1/N	(0.006, 0.77)		

Table 21-1 (Contd). ADSORPTION CONSTANTS FOR SULFATE

Adsorbent			Adsorbate		Electrolyte			Adsorption Measurements		References
Identity (a)	CEC meq/100g	S _A m ² /g	Conc., M		Identity	Conc., M	pH	Constants (b)	Value (c)	
Aiken (untreated)	-	-	10 ^{-3.8}	10 ^{-2.5}	-	-	-	K _F , 1/N	(0.083, 0.65)	Chas et al. 1962c
Treatment 1	-	-	10 ^{-3.8}	10 ^{-2.5}	-	-	-	K _F , 1/N	(0.013-0.026, 0.74-0.81)	
Treatment 2	-	-	10 ^{-3.8}	10 ^{-2.5}	-	-	-	K _F , 1/N	(0.006, 0.70)	
Treatment 3	-	-	10 ^{-3.8}	10 ^{-2.5}	-	-	-	K _F , 1/N	(0.009, 0.64)	
Astoria										
Treatment 1	-	-	10 ^{-3.8}	10 ^{-2.5}	-	-	-	K _F , 1/N	(0.036-0.074, 0.63-0.74)	
Treatment 2	-	-	10 ^{-3.8}	10 ^{-2.5}	-	-	-	K _F , 1/N	(0.007, 0.69)	
Treatment 3	-	-	10 ^{-3.8}	10 ^{-2.5}	-	-	-	K _F , 1/N	(0.044, 0.66)	
Quillayute	-	-	10 ^{-2.6}		Arsenite	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	0	Chas 1964
			10 ^{-2.6}		Borate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	0	
			10 ^{-2.6}		Nitrate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	0	
			10 ^{-2.6}		Silicate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	0	
			10 ^{-2.6}		Chloride	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	0	
			10 ^{-2.6}		Tungstate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	25	
			10 ^{-2.6}		Selenate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	26	
			10 ^{-2.6}		Selenite	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	30	
			10 ^{-2.6}		Vanadate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	34	
			10 ^{-2.6}		Arsenate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	37	
			10 ^{-2.6}		Fluoride	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	41	
			10 ^{-2.6}		Molybdate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	43	
			10 ^{-2.6}		Phosphate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	56	
			10 ^{-2.6}		Acetate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	0	
			10 ^{-2.6}		Succinate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	22	
			10 ^{-2.6}		Malonate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	23	
			10 ^{-2.6}		Citrate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	30	
			10 ^{-2.6}		Maleate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	35	
			10 ^{-2.6}		Versenate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	35	
			10 ^{-2.6}		Thiocyanate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	45	
			10 ^{-2.6}		Malate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	46	
			10 ^{-2.6}		Gluconate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	50	
			10 ^{-2.6}		Tartrate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	58	
			10 ^{-2.6}		Oxalate	0 - 10 ^{-2.7}	4.95	Max ΔA(%)	60	

Table 21-1 (Contd). ADSORPTION CONSTANTS FOR SULFATE

Adsorbent					Adsorbate	Electrolyte			Adsorption Measurements		References
Identity ^(a)			CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants ^(b)	Value ^(c)	
Soil	% Fe ₂ O ₃	% Gibbsite	% Kaolinite	% O.C							
								Soil			
	4	3	25	1.9	0 - 10 ^{-2.6}	KCl	0.02	4.1	A _m , K _L	1.23, 2.80	Conto et al 1979
	6	6	37	0.3	0 - 10 ^{-2.6}	KCl	0.02	4.3	A _m , K _L	5.66, 3.98	
	19	37	9	2.5	0 - 10 ^{-2.6}	KCl	0.02	4.7	A _m , K _L	1.33, 4.00	
	18	33	11	0.7	0 - 10 ^{-2.6}	KCl	0.02	6.0	A _m , K _L	3.75, 4.04	
	16	8	33	2.3	0 - 10 ^{-2.6}	KCl	0.02	5.4	A _m , K _L	0.54, 3.43	
	17	10	43	1.0	0 - 10 ^{-2.6}	KCl	0.02	5.9	A _m , K _L	1.88, 3.94	
Ash soils	Rainfall, mm							Soil			
	200	-	-	-	0 - 10 ^{-2.6}	CaCl ₂	0.01	6.97	A _m , K _L	4.6, 3.7	Hasan 1970
	500	-	-	-	0 - 10 ^{-2.6}	CaCl ₂	0.01	6.60	A _m , K _L	2.6, 4.0	
	1100	-	-	-	0 - 10 ^{-2.6}	CaCl ₂	0.01	5.91	A _m , K _L	6.7, 4.1	
	2300	-	-	-	0 - 10 ^{-2.6}	CaCl ₂	0.01	5.80	A _m , K _L	16.8, 4.1	
	2200	-	-	-	0 - 10 ^{-2.6}	CaCl ₂	0.01	5.20	A _m , K _L	27.7, 4.6	
	4500	-	-	-	0 - 10 ^{-2.6}	CaCl ₂	0.01	6.14	A _m , K _L	43.4, 4.4	

(a) O.M. = organic matter; O.C. = organic carbon

(b) A_m = Langmuir adsorption maximum, $\mu\text{mol g}^{-1}$ K_L = Langmuir constant, $\log \text{M}^{-1}$ A_m^I, K_L^I, A_m^{II}, K_L^{II} = two adsorption sitesA = adsorption, $\mu\text{mol g}^{-1}$ K_{int} = conditional intrinsic adsorption constants funionic species, \log K_{int} = intrinsic adsorption constants funionic species, \log K_F, 1/N = Freundlich constants fun A = K_FC^{1/N}; A, $\mu\text{mol g}^{-1}$; C, μM Max ΔA = maximum percent reduction in adsorption

(c) () = estimated values.

Section 22

VANADIUM

Vanadium (V) is a multivalent element and in aqueous solutions exists in +3, +4, and +5 valence states, each having several hydrolysis products. Vanadium in any of these states does not form strong complexes with other ligands such as F^- , NO_3^- , and SO_4^{2-} . The geochemical behavior of V is poorly understood. However, the available data do suggest a strong affinity of V for iron oxides which may be due to the precipitation of $Fe(VO_3)_2$ and/or adsorption on iron oxides.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIATION

Vanadium can exist in six valence states (from 0 to +5). It can exist in solid state in all six oxidation states. However, in aqueous solutions of environmental range in pH and redox, +3, +4, and +5 valence states are the most stable. The solid phases of V include the metal, oxides, hydroxides, halides, phosphates, sulfates, nitrates, and various solid phases with alkali, alkaline earth, actinide, and transition metal cations. The relative stabilities of these phases depend highly on pH, redox, and activities of other than V ions in the aqueous phase. Known solution species include hydrolysis species, polynuclear complexes (especially for the +5 state), and complexes with F^- , SO_4^{2-} , Cl^- , NO_3^- and other anions. The formation of ion pairs with alkali and alkaline earth cations seems likely, but has not been reported.

The equilibrium constants for reactions involving solids and solution species of V are given in Table A-9. These constants were used to determine the solid phases which could control V solubility and to determine the dominant solution species under a variety of redox potentials. Figure 22-1 is a predominance-area diagram depicting the distribution of V species as a function of redox potential (pe) and pH. No assumptions of solid phases or total concentrations were made; therefore, only the mononuclear species (i.e., one V atom per molecule) were considered. The outlined areas indicate which solution species would predominate under given conditions. The V^{2+} species would not become dominant within the stability region for H_2O . Figure 22-2 illustrates the solubility of the solid (in terms of VO_2^+ concentrations) as a function of pH at a redox potential of $pe + pH = 16$. At low

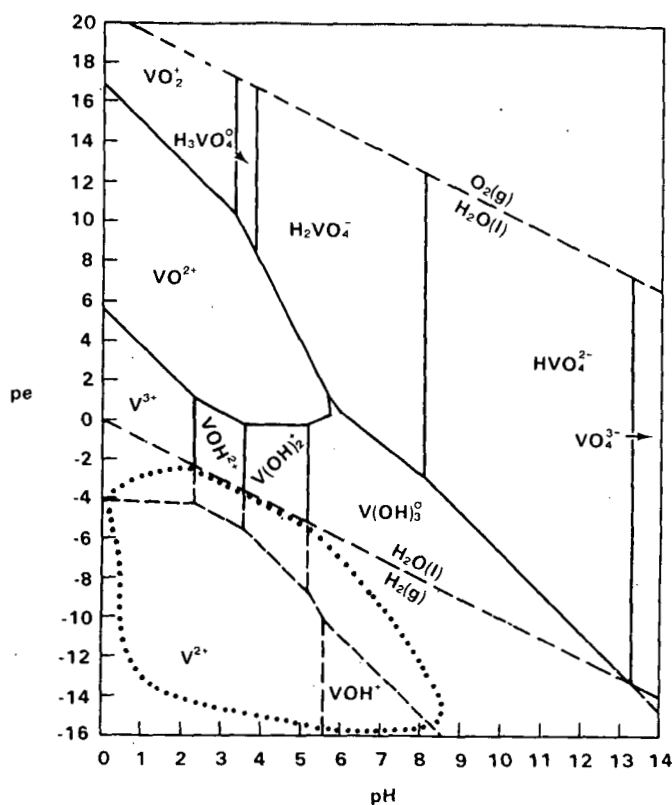


Figure 22-1. The pe-pH Diagram for V-H₂O Systems at 25°C. Dashed lines represent the upper and lower stability limits of water.

pH, $\text{Fe}(\text{VO}_3)_2$ and $\text{V}_2\text{O}_5(\text{c})$ are the least soluble. $\text{Pb}_2\text{V}_2\text{O}_7$ and $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}(\text{c})$ are the least soluble at high pH, depending upon concentrations of accompanying ions.

Figure 22-3 shows the solubility of V minerals (in terms of VO^{2+}) as a function of pH at low redox potential ($\text{pe} + \text{pH} = 7$). $\text{Fe}(\text{VO}_3)_2$ followed by V_2O_4 and V_3O_5 is predicted to be the least soluble up to pH 9, at which point carnotite $[\text{K}_2(\text{VO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}]$ may control solubility. Overall, the solubility of the controlling vanadium solids is apparently greater at low redox potential than at high redox potential.

The distribution of aqueous species as a function of pH in equilibrium with $\text{Fe}(\text{VO}_3)_2$ and $\text{Fe}(\text{OH})_3(\text{am})$ is shown in Figure 22-4 for $\text{pe} + \text{pH} = 7$. The V(IV) species VO^{2+} dominates below pH 6.8 and HVO_4^{3-} dominates pH 6.8. The species V^{3+} , VO_2^+ , and $\text{H}_2\text{V}_2\text{O}_7^-$ are also important under these conditions. Vanadium (V) polynuclear species will become increasingly important at high pH, redox, and V concentrations.

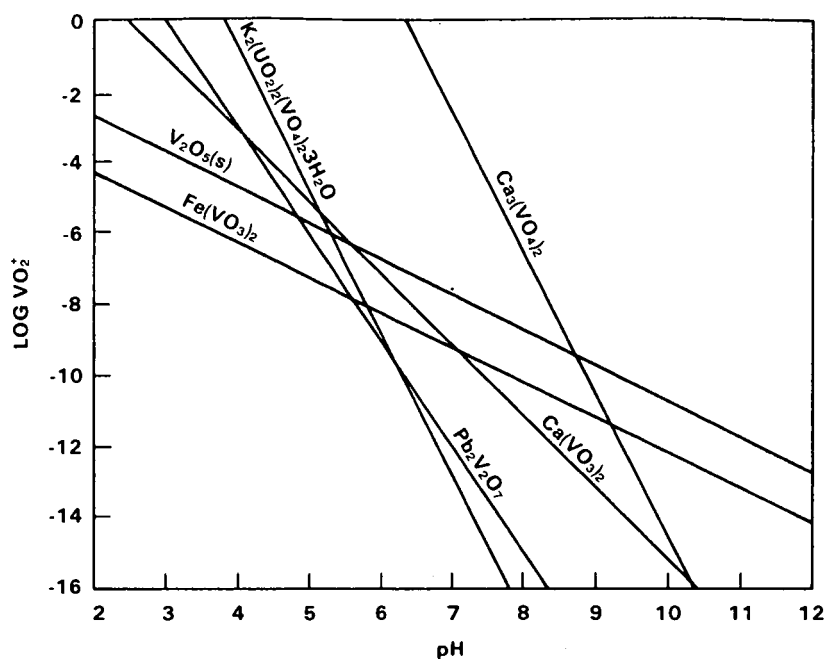


Figure 22-2. Relative solubility of V solids under oxidizing conditions ($pe + pH = 16$) when activity of $UO_2^{2+} = 10^{-12}$, $Ca^{2+} = 10^{-4}$, $K^+ = 10^{-3}$, $Pb^{2+} = 10^{-10}$, and Fe^{2+} controlled by $Fe(OH)_3(am)$.

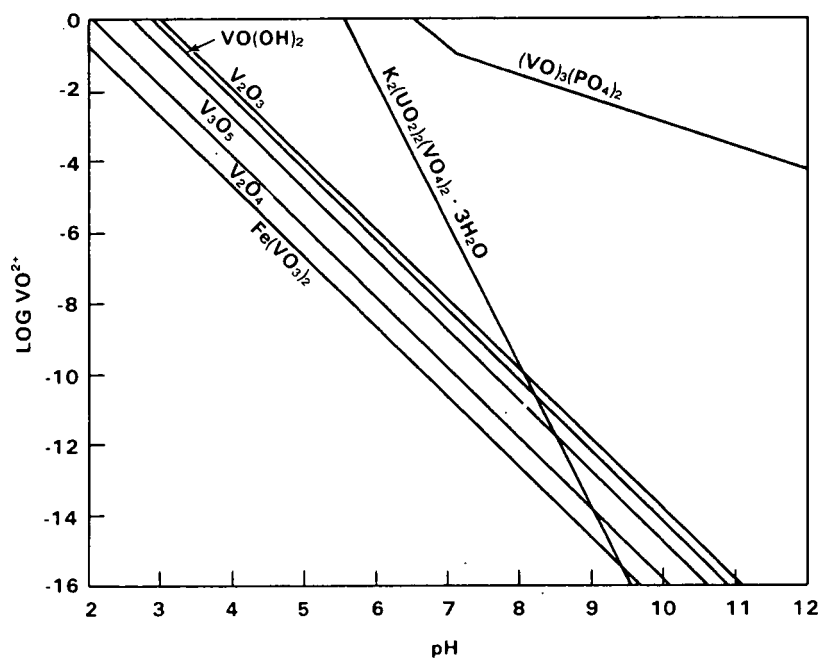


Figure 22-3. Relative solubility of V solids under relatively reducing conditions ($pe + pH = 7$) when total P = 10^{-6} , and activities of $K^+ = 10^{-3}$, $UO_2^{2+} = 10^{-12}$, Fe^{2+} controlled by $Fe(OH)_3(am)$.

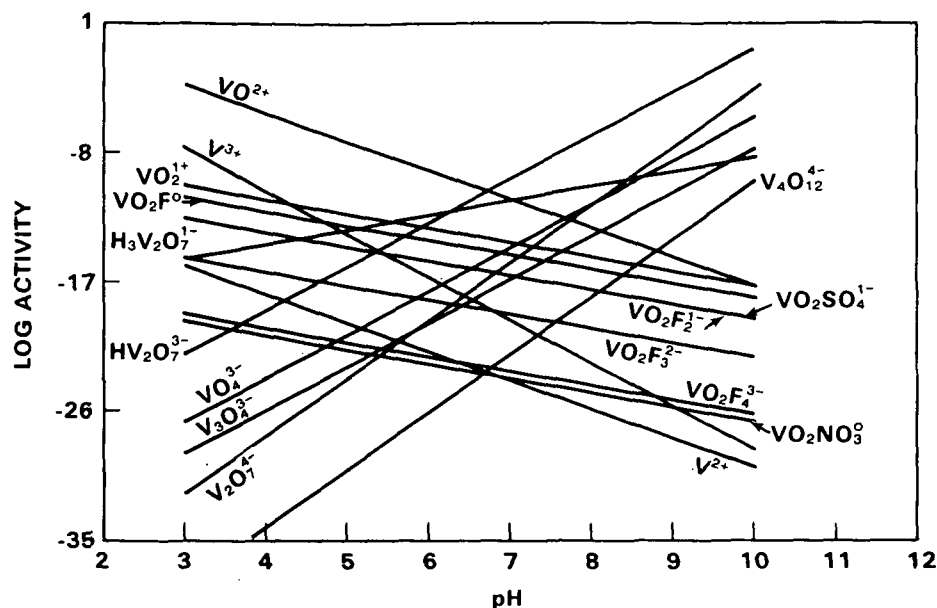


Figure 22-4. Activity of V solution species in equilibrium with $\text{Fe}(\text{VO}_3)_2$, under relatively reducing conditions ($\text{pe} + \text{pH} = 7$).

PRECIPITATION DISSOLUTION

Hem (1977) used thermodynamic data to predict that ferrous vanadate might control V solubilities in natural environments. Physical evidence was not presented. Tenyakov (1965) speculated that the presence of V in secondary Fe minerals may be due to the precipitation of ferric vanadates. Taylor and Giles (1970) point out many structural similarities between V solids and Fe solids: V_2O_3 (karelionite) is isostructural with Fe_2O_3 (harmatite) and montroseite ($\text{V, Fe} \text{ OOH}$) is isostructural with $\gamma\text{-FeOOH}$ (goethite). These similarities suggest the ease with which V could substitute for Fe in the ferric oxide lattices.

McBride (1979) used electron spin resonance to examine the adsorption of VO^{2+} on smectite surfaces. The clay tended to promote hydrolysis of the VO^{2+} , and McBride suggested the possible formation of the solid $\text{VO}(\text{OH})_2 \cdot n\text{H}_2\text{O}$.

ADSORPTION/DESORPTION

Literature describing the adsorption of vanadium in soils or soil constituents is limited and little pertinent data are available. Below pH 8, the V(IV) and V(V) valence states dominate under oxidizing conditions (Figure 22-1). Electron spin resonance studies indicate that the VO^{2+} ion adsorbs in smectite surfaces primarily in the hydrolyzed forms (McBride 1979). However, it is also possible that

vanadyl(IV) may be adsorbed by Mn- or Fe-oxides and oxidized to vanadate(V) (Hem 1977, Taylor and Giles 1970). The distribution of V in some soils closely follows the distribution of Fe, and more importantly, secondary iron oxides (Turton et al. 1961,1962) indicating their importance as adsorbents for V. Vanadium is mobilized by soluble soil organic matter under both aerobic and anaerobic conditions and V(V) is readily reduced to V(IV) and complexed in the presence of organic matter at reduced O_2 levels (Bloomfield and Kelso 1973).

Section 23

ZINC

The dominant zinc (Zn) solution species in groundwaters at pH values <8.2 and containing $<10^{-2.5}$ M SO_4^{2-} activity is Zn^{2+} . The precipitation/dissolution attenuation mechanism has not been adequately studied. Most all of the available information is coincidentally developed during adsorption studies that used fairly high concentrations of Zn. As a result, $\text{Zn}(\text{OH})_2$ has often been indicated as the solubility controlling solid. Willemite and Zn-carbonates ($\text{ZnCO}_3 \cdot \text{H}_2\text{O}$ or ZnCO_3) have also been reported as possible solubility-controlling solids. Because most of the available adsorption/desorption data were obtained with high Zn concentrations, these studies are not directly applicable to utility waste disposal where low Zn concentrations are expected. At low Zn concentrations ($<10^{-5}$ M), Zn is specifically adsorbed by Fe, Al, and Mn-oxides. At higher Zn concentrations, nonspecific adsorption is the controlling adsorption mechanism. The effects of competing and complexing ligands have not been well studied although some of the available information indicates that cations such as Mg^{2+} and Cd^{2+} may compete with Zn for specific adsorption sites while specifically bound anions such as SO_4^{2-} , CrO_4^{2-} , SeO_3^{2-} , AsO_4^{3-} , PO_4^{3-} may enhance zinc adsorption.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIES

Zinc in natural aqueous environments exists exclusively as +2 valence state. Lindsay (1979) calculated the relative solubility of Zn compounds. His results showed that franklinite (ZnFe_2O_4) and willemite (Zn_2SiO_4) are the two least soluble Zn compounds. Lindsay and Norvell (1969) and Norvell and Lindsay (1970) studied Zn equilibria in a few soils and observed that Zn concentrations appeared to be solubility controlled by an unidentified Zn compound, which Lindsay (1979) called soil-Zn. The soil-Zn solubility is intermediate to franklinite and willemite. Both willemite and franklinite are relatively high temperature minerals and are not expected to form in soils. Other Zn minerals such as $\text{Zn}(\text{OH})_2$, ZnCO_3 , and ZnO are relatively more soluble than willemite and franklinite.

To determine the relative abundance of Zn(II) species in groundwater representative of utility waste environment, activities of different Zn species in equilibrium

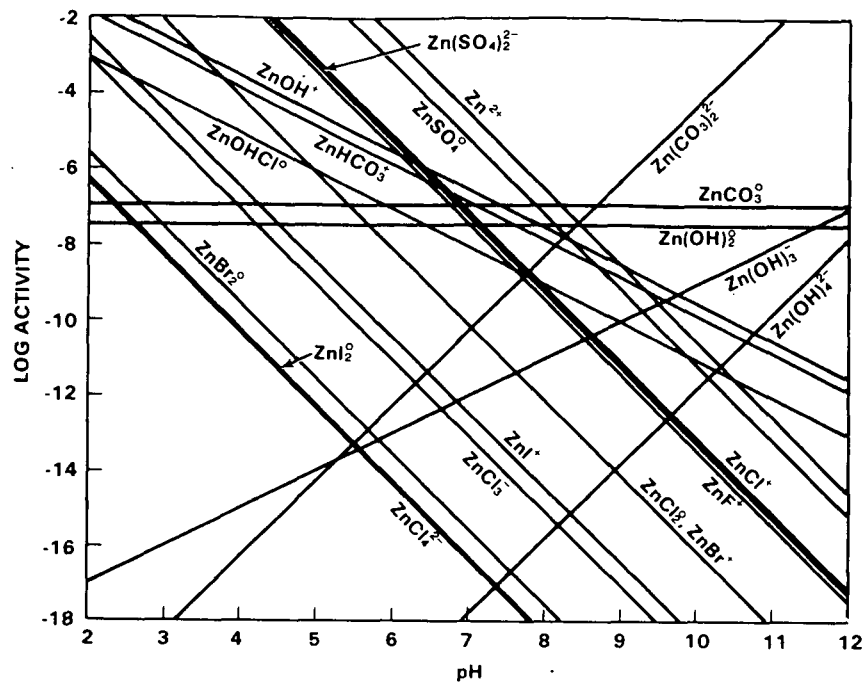


Figure 23-1. Activities of different Zn species in equilibrium with willemite (ZnSiO_4) when activities of $\text{SO}_4^{2-} = \text{Cl}^- = 10^{-3}$, $\text{NO}_3^- = \text{F}^- = 10^{-4}$, $\text{Br}^- = \text{I}^- = 10^{-5}$, and $\text{CO}_2(\text{gas}) = 10^{-3.52}$ atmosphere.

with willemite (Zn_2SiO_4) were plotted (Figure 23-1) using the thermodynamic data contained in the geochemical model MINTEQ (Felmy et al. 1980). Under the assumed groundwater compositions (Figure 23-1), Zn^{2+} followed by ZnSO_4^0 are the dominant aqueous species groundwaters of pH values < 8.2 . At pH values > 8.2 , Zn carbonate species are dominant. Other complexes of Zn with Cl^- , F^- , Br^- , OH^- , and I^- do not contribute significantly to the total Zn in solution.

PRECIPITATION/DISSOLUTION

Except for soil-Zn (Lindsay 1979), no solubility-controlling solids have been reported in natural soils and sediments. Jenne et al. (1980) modeled waters of the Missouri tri-state mining area and reported that the concentration of Zn appeared to be controlled by $\text{ZnCO}_3 \cdot \text{H}_2\text{O}$ or ZnCO_3 . They also suggested that Zn_2SiO_4 may also be the solubility-controlling phase.

During laboratory adsorption experiments, many authors used fairly high concentrations of Zn (10^{-4} to 10^{-2} M) and reported that under high pH the concentration of Zn may have been controlled by the Zn(OH)_2 or ZnCO_3 . Singh and Sekhon (1977) observed

that, under alkaline conditions, Zn concentrations in several soils exceeded the solubility product of $\text{Zn}(\text{OH})_2$ when $1.5 \times 10^{-3} \text{ M}$ Zn was added to these soils. Trehan and Sekhon (1977) indicate that $\text{Zn}(\text{OH})_2$ or ZnCO_3 may be the soluble Zn controlling solids in calcareous soils amended with $4.6 \times 10^{-4} \text{ M}$ Zn. Kinniburgh and Jackson (1982) studied the adsorption of Zn by Fe gel for 10^{-2} to 10^{-4} M Zn solutions in 1 M NaNO_3 . They reported that, at pH 6.5 and initial 10^{-2} M Zn, the reproducibility of adsorption was relatively poor which they attributed to the possible precipitation of zinc hydroxide or hydroxycarbonate. Bolland et al. (1977) observed a marked removal of Zn (nearly zero percent at pH 7.3 to about 80% at pH 8) from $4 \times 10^{-2} \text{ M}$ Zn in 0.1 M NaCl which they attributed to precipitation of Zn solids.

Kuo and Mikkelsen (1979) observed that adsorbed Zn on soils became more strongly bonded to the solid phase with time. This increase in the stability of adsorbed zinc has been attributed to recrystallization of the adsorbed phase into a nonadsorbed solid phase. Loganathan et al. (1977) studied the adsorption of Zn^{2+} on $\delta\text{-MnO}_2$. Results of electrophoretic mobility measurements suggested that at high pH, the $\delta\text{-MnO}_2$ surface behaved as though Zn^{2+} was forming a surface coverage of $\text{Zn}(\text{OH})_2(\text{s})$.

ADSORPTION/DESORPTION

Like other cationic heavy metals, zinc is adsorbed specifically and by ion exchange (Table 23-1). Above Zn solution concentrations sufficient to saturate specific adsorption sites, Zn is adsorbed by simple coulombic interaction with cation exchange sites. Hence, the predominant adsorbents controlling the adsorption behavior of Zn in soils are Mn and Fe oxides (Takematsu 1979; Shuman 1977; Dempsey and Singer 1980; Kinniburgh and Jackson 1982; McKenzie 1980; Bruinix 1975, Bolland et al. 1977; Bar-Yosef et al. 1975; Balistrieri and Murray 1982; Benjamin and Leckie 1981a; Forbes et al. 1976; Gadde and Laitinen 1974; Loganathan et al. 1977; Rophael et al. 1979; Kinniburgh et al. 1977) with lesser contribution from soil organic matter (Kuo and Mikkelsen 1979; Bunzl et al. 1976) and clay minerals (Farrah and Pickering 1977; Wada and Kakuto 1980; Takematsu 1979; Frost and Griffin 1977; Stuanes 1976). Many studies of Zn adsorption by soil were conducted using high concentrations of Zn (Trehan and Sekhan 1977; Singh and Sekhon 1977; Sidhu et al. 1977; Kuo and Mikkelsen 1979; Shukla et al. 1980; Sidle and Kardos 1977; Shuman 1976; Clarke and Graham 1968; Bar-Yosef 1979) which exceed normal environmental concentrations and those of immediate relevance to utility waste disposal. Under these conditions, Zn adsorption correlates with cation exchange capacity or clay content (Trehan and Sekhon 1977; Singh and Sekhon 1977; Sidhu et al. 1977; Shuman 1976; Duddridge and Wainwright 1981) and is retained by coulombic interaction rather than specific adsorption.

Zinc ($<10^{-4.5}$ M) adsorption displays marked pH depending on silica (Benjamin and Leckie 1980), iron oxides (Benjamin and Leckie 1980; Balistrieri and Murray 1982; Gadde and Laitinen 1974; McKenzie 1980; Kinniburgh and Jackson 1982; Benjamin and Leckie 1981a). Mn oxides (Gadde and Laitinen 1974; McKenzie 1980; Loganathan et al. 1977), Al oxides (Benjamin and Leckie 1980) and soil. This arises from the aqueous hydrolysis of Zn and the amphoteric nature of oxide and hydrous oxide minerals. Under comparable experimental conditions, the Zn adsorption edge falls at higher pH than that of Cu and Pb on iron (Balistrieri and Murray 1982; Benjamin and Leckie 1981a; McKenzie 1980) and Mn oxides (McKenzie 1980; Loganathan and Burua 1973) suggesting that Zn is less strongly adsorbed. In contrast, Zn is more strongly adsorbed than: 1) Cd, Co, Ni, and Mn by Fe oxides (Benjamin and Leckie 1981a; McKenzie 1980); 2) Cd by Al oxides (Benjamin and Leckie 1980); and 3) Ni by Mn oxides (McKenzie 1980). The pH dependency of Zn adsorption decreases at higher solution concentrations of Zn (Wada and Kakuto 1980; Shuman 1977) and when clay minerals are used as adsorbents (Wada and Kakuto 1980; Frost and Griffin 1977; Hatton and Pickering 1980).

The presence of competing cationic constituents may, under some conditions, reduce the specific adsorption and ion exchange of Zn in soil. Divalent alkaline earths (Mg^{2+} , Ca^{2+}) in high concentration ($>10^{-3}$ M) compete with Zn for ion exchange sites in soils (Shukla et al. 1980) and on clay minerals (Farrah and Pickering 1977, Stuanes 1976) and for specific adsorption sites on Fe oxides (Balistrieri and Murray 1982). Ion exchange selectivity measurements, however, indicate that Zn is strongly preferred over Ca by clay minerals when Ca is present in lower concentration ($<10^{-4}$) (Wada and Kakuto 1980). Zinc, Cu, Pb, and Cd in comparable concentrations (10^{-6} M) do not compete for specific adsorption sites on goethite (Balistrieri and Murray 1982) or amorphous Fe oxyhydroxide (Benjamin and Leckie 1981b) suggesting that preferential adsorption sites exist on these solids for each metal. Though Zn is more strongly adsorbed, Zn and Cd may compete for the same adsorption site on limonite (γ -FeOOH) and aluminum oxide (γ -Al₂O₃) (Benjamin and Leckie 1980).

The effects of strongly complexing anions on Zn adsorption has not been studied in detail; however, the nonspecifically adsorbed, noncomplexing monovalent anions (NO_3^- , Cl^- , ClO_4^-) have little effect on Zn adsorption (Balistrieri and Murray 1982; Ball et al. 1980; and Bolland et al. 1977). Specifically adsorbed anions (e.g., SO_4^{2-} , CrO_4^{2-} , SeO_4^{2-} , AsO_4^{3-} , PO_4^{3-}) may enhance Zn adsorption by Fe oxides (Bolland et al. 1977; Balistrieri and Murray 1982; Benjamin and Bloom 1982), possibly by reduction in net surface positive charge.

Measurement of proton release during adsorption of Zn on hydrous and crystalline oxides affirms the specific adsorption process. At low adsorption density, i.e., adsorption from solutions containing $<10^{-6}$ M Zn, the number of protons released for each ionic species adsorbed by Fe, Mn, Al oxides is generally >1.5 (Kinniburgh and Jackson 1982; Bruniux 1975; Balistrieri and Murray 1982; Kinniburgh et al. 1977; James and McNaughton 1977; Kalbasi et al. 1978). The release of protons can be described by the reactions



These reactions have been used, in combination with the pH dependent electrostatic properties of the solid surface, to model Zn adsorption on Fe and Al oxides (Balistrieri and Murray 1982; Benjamin and Leckie 1980; Benjamin and Bloom 1982; Barrow et al. 1981). The monovalent species, ZnOH^+ , appears to be adsorbed in preference to Zn^{2+} at all pH values (Bolland et al. 1977; Balistrieri and Murray 1982; Barrow et al. 1981). Not only is the solvation energy less for ZnOH^+ , but the electrostatic repulsion between positive surfaces and ZnOH^+ is smaller. The affinity of surface for ZnOH^+ appears to be high enough to induce ZnOH^+ formation and adsorption in spite of very low solution concentrations below pH 7.5.

Both the Langmuir (Kuo and Mikkelsen 1979; Shuman 1977; Sidhu et al. 1977; Singh and Sekhon 1977; Trehan and Sekhon 1977) and Freundlich (Kuo and Mikkelsen 1979) equations are used to describe Zn adsorption in soil. When large concentration gradients of Zn are used, multiple regions of linearity are often observed in the Langmuir isotherms. These are ascribed to different adsorption sites (Shuman 1975), likely reflecting Zn retention by specific adsorption and cation exchange mechanisms.

Table 23-1. ADSORPTION CONSTANTS FOR ZINC

Absorbent			Adsorbate	Electrolyte			Adsorption Measurements		References
Identity (a)	CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
Clay Minerals									
Montmorillonite	---	---	10 ^{-3.8}	---	---	5	K ^{Zn} _{Ca}	0.2	Farrah and Pickering 1977
Na-saturated							K ^{Zn} _{Cd}	0.9	
							K ^{Zn} _{Mg}	0.7	
							K ^{Zn} _{Cu}	0.6	
							K ^{Pb} _{Db}	0.3	
	"Free: Fe ₂ O ₃ , %								
Montmorillonite	69	2.13	10 ^{-6.6}	CaCl ₂	10 ^{-2.4}	6.9	K ^{Zn} _{Ca}	158	
Halloysite			10 ^{-4.7}	"	10 ^{-2.3}	4.9	"	1.5	
Ca-Saturated	6.6	0.11	10 ^{-6.6}	"	10 ^{-3.4}	7.0	"	310	
Mavi			10 ^{-5.0}	"	10 ^{-3.1}	6.4	"	19	
			10 ^{-4.4}	"	10 ^{-3.0}	4.9	"	5.7	
Chozo	43.3	3.76	10 ^{-6.2}	"	10 ^{-3.0}	6.9	"	260	
"			10 ^{-3.9}	"	10 ^{-2.5}	5.1	"	6.4	
Uenae	56.7	2.17	10 ⁻⁶	"	10 ^{-2.8}	7.0	"	243	
"			10 ^{-4.3}	"	10 ^{-2.4}	5.9	"	19	
"			10 ^{-3.5}	"	10 ^{-2.3}	4.7	"	11	
Yoake	14.2	0.75	10 ⁻⁷	"	10 ^{-3.6}	6.8	"	86	
"			10 ^{-6.5}	"	10 ^{-7.1}	6.0	"	73	
"			10 ^{-5.8}	"	10 ^{-3.0}	5.3	"	21	
Naegi	7.7	0.91	10 ^{-6.3}	"	10 ^{-3.4}	6.7	"	31	
"			10 ^{-4.9}	"	10 ^{-3.3}	6.1	"	1.1	
Clay Minerals									
Reductant-treated red clay	---	67	10 ^{-7.8} 10 ^{-5.8}	Seawater	~0.7	8	A _m , K _L	(1.2, 6.2)	Takematsu 1979
Montmorillonite, untreated	---	100	"	"	"	"	K _d	2	
Na-Saturated							K _d	2	
Montmorillonite,	---	---	10 ^{-3.6} -10 ^{-2.6}	Landfill	~0.1	5	A _m , K _L	(29, 3.0)	Frost and Griffin 1977
Ca-Saturated			"	leachate	"	6	"	(35, 3.1)	
Kaolinite,	---	---	"	"	"	5	"	(2.7, 3.6)	
Ca-Saturated			"	"	"	6	"	(5.5, 3.5)	

Table 23-1 (Contd). ADSORPTION CONSTANTS FOR ZINC

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		References
Identity (a)	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
Clay Minerals (contd)									
Montmorillonite	70	---	10 ^{-2.3} -10 ^{-1.3}	ΣCl ⁻	0.01-0.1	5-6	A _m , K _L	(450, 2.9)	Stuanes 1976
					0.1		K _{Mn} ^{Zn}	1.33-1.75	
					0.01		"	1.77-1.88	
					0.1		K _{Cd} ^{Zn}	2.04-2.25	
					0.01		"	1.62-1.70	
					0.1		K _{Hg} ^{Zn}	247 - ∞	
					0.01		"	99 - ∞	
Kaolinite	4.0	---	10 ^{-2.3} -10 ^{-1.3}	ΣCl ⁻	0.01-0.1		A _m , K _L	(18, 2.7)	
					0.1		K _{Mn} ^{Zn}	1.18-1.27	
					0.01		"	1.18-1.27	
					0.1		K _{Cd} ^{Zn}	1.25-1.54	
					0.01		"	1.25-1.54	
					0.1		K _{Hg} ^{Zn}	10.5-34.5	
					0.01		"	10.5-34.5	
Vermiculite	70	---	10 ^{-2.3} -10 ^{-1.3}	ΣCl ⁻	0.01-0.1	5-6	A _m , K _L	(500, 3.0)	Stuanes 1976
					0.1		K _{Mn} ^{Zn}	3.35-4.55	
					0.01		"	3.35-4.55	
					0.1		K _{Cd} ^{Zn}	3.83-5.54	
					0.01		"	4.39-5.82	
					0.1		K _{Hg} ^{Zn}	247 - ∞	
					0.01		"	247 - ∞	
Montmorillonite	96	--	10 ^{-2.3} -10 ^{-1.3}	--	--	--	A _m , K _L	(560, 2.7)	
Feldspars:									
Albite	>0.6	---	"	--	--	--	"	(6.1, 3.3)	
Labradorite	<2.5	---	"	--	--	--	"	(83, 2.8)	
Silica									
α - SiO ₂	---	---	10 ⁻⁶	---	---	---	K ^{Int} _{ZnOH}	7.5	Davis and Leckie 1978

Table 23-1 (Contd). ADSORPTION CONSTANTS FOR ZINC

Adsorbent			Adsorbate	Electrolyte			Adsorption Measurements		References
Identity (a)	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
Alumina									
Al hydrous oxide									
Fresh	493	441	10 ^{-4.5} - 10 ⁻³	Na ₂ SO ₄	0.01	---	A _m , K _L	160, 6.2	Shuman 1977
Aged	52	59	"	"	"	---		15, 4.3	
γ-Al ₂ O ₃	---	---	10 ^{-6.3}	---	---	---	K _{ZnOH} ^{Int}	10.1	Davis and Leckie 1978
Fe-Oxides									
Fe(OH) ₃ (am)	---	600	10 ^{-6.7} -10 ⁻⁵	---	---	6 7 8	A _m , K _L " " ΔG ^o _{chem}	25, 5.4 170, 5.9 440, 6.7 -13.1	Dempsey and Singer 1980
Fe(OH) ₃ (am)	600	---	---	---	---	---	*K _{Zn} ^{Int} , *K _{ZnOH} ^{Int}	-2.3, -10.5	Dempsey and Singer 1980
Fe hydrous oxide	---	---	10 ⁻⁶ - 10 ^{-3.1}	NaNO ₃	1.0	5.5	K _{Zn} ^{Int} , K _{ZnOH} ^{Int} K _{F,1/N}	(8.3, 9.1) 0.81, 0.70	
"	---	---	10 ^{-3.1} - 10 ⁻²			5.5		3.24, 0.49	
"	---	---	10 ⁻⁶ - 10 ^{-3.1}			6.5		15.4, 0.56	
Fresh	354	303	0 - 10 ^{-6.3}	Na ₂ SO ₄	0.01	---	A _m , K _L	160, 5.7	Shuman 1977
Aged	8	29	"	"	"	---		14, 4.3	
Hydrated Fe Oxide	---	215	10 ^{-7.8} - 10 ^{-5.8}	Seawater	~0.7	8	A _m , K _L K _d	(600, 5.9) 500	Takematsu 1979
Goethite	---	75	0 - 10 ⁻³	KNO ₃	0.1	5	A _m , K _L A _m , K _L	(39, 2.7)	McKenzie 1980
Hematite	---	20	0 - 10 ⁻³	"	0.1	"	A _m , K _L K _d	(8, 3.1)	
Fe(OH) ₃ , coprecip.	---	---	10 ^{-5.4}	KNO ₃	0.01	8.5	K _d	1.3	Bruinix 1975
			"	Syn. River H ₂ O	---	"	"	1.3	
			"	Seawater	---	"	"	0.9	
							K _{F,1/N}	23.9, 0.54	
Goethite	---	73	10 ^{-4.3} - 10 ^{-2.9}	NaCl	0.1	5	A _m , K _L	(5.9, 4.5)	Bolland et al. 1977
						6	"	(68, 3.8)	
						7	"	(64, 4.1)	

Table 23-1 (Contd). ADSORPTION CONSTANTS FOR ZINC

Adsorbent			Adsorbate		Electrolyte		Adsorption Measurements		References
Identity ^(a)	CEC meq/100g	S _g A _g m ² /g	Conc., M	Identity	Conc., M	pH	Constants ^(b)	Value ^(c)	
Fe Oxides (contd)									
Goethite	---	65-80	---	NaCl	0.1	---	K _{Zn} ,	6.0	Bar-Yosef et al. 1975
	---			NaClO ₄	0.16	---	K _{ZnOH}	7.4	
	---			NaAc/HAc	0.16	---	K _{Zn} ,	5.7	
							K _{ZnOH}	7.1	
							K _{Zn} ,	5.3	
							K _{ZnOH} ,	8.7	
							K _{ZnAC}	4.7	
			10 ^{-5.7} -10 ^{-3.7}	NaCl	0.1	5.0	A _m , K _L ,	(5,4.1)	
			"	"	"	6.0	"	(51,4.0)	
					6.5	"	(74,4.2)		
Goethite	---	65-80	10 ^{-5.7} -10 ^{-3.7}	NaClO ₄	0.16	6.0	A _m , K _L	(28, 4.2)	Balistrieri and Murray 1982
			"	NaAC/HAc	0.16	6.5	"	(71, 4.2)	
				"	"	5.0	A _m , K _L	(6, 4.4)	
				"	"	6.0	"	(55, 4.1)	
	---	51.8		"	"	7.5	"	(103, 4.2)	
	---	51.8	10 ^{-6.3} - 10 ^{-4.5}	Seawater	~0.7	5-8	*K _{anOH} ^{Int}	9.15	
Fe ₂ O ₃ -H ₂ O(Am)	---	---	10 ^{-7.5} -10 ^{-4.0}	NaNO ₃	0.01	6.4	K _{ZnOH} ^{Int}	(10.2)	Benjamin and Leckie 1981a
							K _F , 1/N	8.9, 1.0	
							K _E	-16.9	
Goethite	---	---	10 ^{-6.3}	---	---	---	K _{ZnOH} ^{Int}	9.4	Davis and Leckie 1978
	---	---	10 ^{-4.5}	NaNO ₃	0.08	6-8	K _C ⁱ	-3.3	
									Forbes et al. 1976

Table 23-1 (Contd). ADSORPTION CONSTANTS FOR ZINC

Adsorbent			Adsorbate		Electrolyte		Adsorption Measurements		References
Identity ^(a)	CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants ^(b)	Value ^(c)	
<u>Mn Oxides</u>									
MnO _x (MnO _{1.90})	---	260	10 ^{-6.2} -10 ^{-4.7}	---	---	6.0	A _m , K _L	1170, 6.1	Dempsey and Singer 1980
			"	---	---	7.0	"	1590, 6.3	
			"	---	---	8.0	"	2960, 5.8	
						8.5	ΔG _{Chem} ^o	4640, 5.8 -2.6	
Hydrous Mn oxide	---	---	10 ⁻⁴ -10 ^{-2.5}	---	---	6.0	A _m , K _L	(2760, <4)	Gadde and Laitinen 1974
δ-MnO ₂	---	160	10 ^{-4.3} -10 ^{-2.9}	NaNO ₃	10 ⁻³	4.0	A _m , K _L	(1020, 3.7)	Loganathan and Burau 1973
δ-MnO ₂	---	98	10 ⁻³ -10 ^{-2.2}	KNO ₃	0.1	5	A _m , K _L	(1020, 3.8)	McKenzie 1980
α-MnO ₂ , K ₂ Mn ₈ O ₁₆	---	206	"	"	"	"	"	(710, 3.4)	
δ-MnO ₂	---	160	10 ⁻⁴ -10 ⁻³	NaNO ₃	10 ⁻³	5 6	A _m , K _L	(1650, 3.8) (2420, 4.0)	Loganathan et al. 1977
<u>Mn Oxides</u>									
γ-MnOOH	---	---	10 ⁻⁸ - 10 ⁻⁶	Seawater	~0.7	8	A _m , K _L	(34, 6.2)	Takematsu 1979
7A MnO ₂	---	---	"	"	"	"	K _d	20	
δ-MnO ₂	---	---	"	"	"	"	K _d	200	
							A _m , K _L	(1680, 6.2)	
MnO ₂	---	2.3	0.01	---	---	6.0	K _d	800	Rophael et al. 1979
+0.1% Li ⁺	---	4.6	"	---	---	6.6	"	300	
+0.2% V(V)	---	1.7	"	---	---	2.0	"	450	
+0.1% Mo(VI)	---	3.2	"	---	---	5.1	"	830	
<u>Miscellaneous</u>									
Calcite	---	6.78	10 ⁻⁷ - 10 ^{-5.3}	---	---	8.4	A _m , K _L	(59, 5.2)	Jurinak and Bauer 1956
							ΔG _{ADS} ^o	-8.5	
Dolomite (Mg/Ca = 0.87)	---	11.9	"	---	---	8.6	A _m , K _L	(119, 5.6)	
							ΔG _{ads} ^o	-8.6	
Ca-Magnesite	---	25.8	"	---	---	8.9	A _m , K _L	(58, 6.3)	
(Mg/Ca = 17.3)							ΔG _{ads} ^o	-8.9	
<u>Organic Matter</u>									
Soil humic acid	---	---	10 ^{-4.3} - 10 ^{-2.3}	---	---	2.4	A _m , K _L	(12, 3.4)	Kerndoff and Schnitzer 1980
Peat	---	---	10 ^{-4.6} - 10 ^{-2.6}	---	---	---	A _m , K _L	(180, 5.0)	Bunzl et al. 1976

Table 23-1 (Contd). ADSORPTION CONSTANTS FOR ZINC

Adsorbent				Adsorbate		Electrolyte			Adsorption Measurements		References
Identity (a)			CEC meq/100g	S ₂ A ₂ m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (c)	
Soil	% Clay	% O.M.									
	14.0	0.52	10.9	---	10 ^{-4.5} -10 ^{-3.3}	CaCl ₂	0.1	---	A _m , K _L	31.8, 4.9	Trehan and Sekhon 1977
	14.0	0.37	9.3	---	"	"	"	"	"	36.4, 5.0	
	20.0	0.84	11.1	---	"	"	"	"	"	63.6, 5.0	
	21.3	1.23	15.1	---	"	"	"	"	"	10.6, 4.9	
	15.0	0.98	14.9	---	"	"	"	"	"	4.7, 5.0	
	3.9	0.27	3.8	---	"	"	"	"	"	19.1, 5.0	
	10.1	0.61	6.96	---	10 ^{-4.1} -10 ^{-2.8}	KCl	0.1	7.0	A _m , K _L	16.5, 3.5	Singh and Sekhon 1977
	31.2	1.26	18.2	---	"	"	"	"	"	49.0, 3.6	
	10.4	0.69	6.09	---	"	"	"	"	"	14.5, 3.7	
	24.6	0.75	12.18	---	"	"	"	"	"	31.5, 3.6	
	20.2	0.76	10.44	---	"	"	"	"	"	24.0, 3.4	
	5.5	0.33	3.83	---	"	"	"	"	"	11.5, 3.4	
	8.9	0.34	4.35	---	"	"	"	"	"	14.5, 3.4	
Loam	28.0	0.28	10.0	---	10 ^{-4.3} -10 ^{-3.1}	CaCl ₂	0.01	9.2	T(°C), A _m , K _L	17, 3.3, 4.8	Sidhu et al. 1977
				---	"	"	"	"	"	30, 3.6, 4.6	
				---	"	"	"	"	"	40, 3.9, 4.4	
Sand	9.00	0.18	3.50	---	"	"	"	8.1	"	30, 0.89, 4.2	
Loamy sand	12.0	0.17	3.75	---	"	"	"	8.4	"	30, 1.04, 5.0	
Sandy loam	17.0	0.27	5.10	---	"	"	"	8.4	"	17, 1.7, 4.8	
				---	"	"	"	"	"	30, 1.8, 4.6	
				---	"	"	"	"	"	40, 1.6, 4.5	
Clay loam	9.2	0.6	---	---	0 - 10 ^{-5.5}	CaCl ₂	0.016	7.7	A _m , K _L	(9.4, 5.5,	Kuo and Mikkelsen 1979
				---	"	"	"	"	K _F , 1/N	1.8, 0.94)	
				---	>10 ^{-5.5}	"	"	"	K _F , 1/N	(3.8, 0.32)	
Clay	49.0	1.0	---	---	0-10 ^{-5.8}	"	"	8.5	A _m , K _L	(24, 5.8,	
				---	>10 ^{-5.8}	"	"	"	K _F , 1/N	13, 0.85)	
				---		"	"	"	K _F , 1/N	(15, 0.37)	
Loamy sand, Untreated	-	0.36	8.21	---	10 ⁻⁶ - 0.1	---	---	8.3	K _F , 1/N	(0.46, 0.46)	Shukla et al. 1980
Ca-saturated				---	"	---	---	7.8		(0.45, 0.46)	
Mg-				---	"	---	---	7.8		(0.47, 0.45)	
Na-				---	"	---	---	9.3		(0.96, 0.41)	
K-				---	"	---	---	9.3		(0.62, 0.45)	
H-				---	"	---	---	2.8		(0.41, 0.47)	

Table 23-1 (Contd). ADSORPTION CONSTANTS FOR ZINC

Adsorbent				Adsorbate	Electrolyte			Adsorption Measurements		References
Identity (a)		CEC meq/100g	S ₂ A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants (b)	Value (b)	
Soil (wt)	% O.M.									
Loam,	0.28	5.36	---	10 ⁻⁶ -0.1	---	---	8.5			
Untreated				"	---	---		K _F , 1/N	(0.88, 0.44)	Shukla et al. 1980
Ca-saturated				"	---	---	7.8	"	(1.40, 0.39)	
Mg-				"	---	---	7.8	"	(1.39, 0.39)	
Na-				"	---	---	9.3	"	(4.29, 0.32)	
K-				"	---	---	9.3	"	(1.39, 0.39)	
H-				"	---	---	2.8	"	(0.28, 0.58)	
								AG _{ex} ⁰ , Ca-Zn	41.3	
								" , Mg-Zn	41.5	
								" , K-Zn	31.3	
								" , Na-Zn	23.6	
Soil	% O.M.									
Clay loam (forest soil)							Soil			
0.75 cm	10.6	18.4	---	10 ^{-5.1} -10 ^{-3.5}	Sewage	---	6.4	A _m , K _L	(4.3, 7.2)	Sidle and Kardos 1977
7.5 - 15 cm	5.4	8.4	---	"	sludge leachate	---	5.4		(1.7, 7.5)	
Clay loam										
A 1. Untreated clay fraction		23.8	264	0-10 ^{-3.31}	Na ₂ SO ₄	0.01	6.0	A _m , K _L	66, 4.7	Shuman 1975
2. Fe oxides removed		27.4	287	"	"	"	"		66, 4.5	
B2 1.		13.7	162	"	"	"	"	58, 4.4		
2.		17.6	204	"	"	"	"	28, 4.5		
Sandy loam										
A 1.		6.4	111	"	"	"	"	"	35, 4.5	
2.		10.1	71	"	"	"	"	"	63, 4.6	
B2 1.		15.7	156	"	"	"	"	"	28, 4.5	
2.		19.1	517	"	"	"	"	"	29, 4.5	
Loamy sand										
A 1.		17.8	132	"	"	"	"	"	21, 4.6	
2.		13.9	124	"	"	"	"	"	18, 4.6	
B2 1.		14.8	150	"	"	"	"	"	30, 4.6	
2.		18.2	504	"	"	"	"	"	33, 4.5	
Loamy sand										
A 1.		25.8	223	"	"	"	"	"	51, 4.5	
2.		23.1	220	"	"	"	"	"	72, 4.4	
B2 1.		---	256	"	"	"	"	"	74, 4.6	
2.		28.5	232	"	"	"	"	"	87, 4.5	

Table 23-1 (Contd). ADSORPTION CONSTANTS FOR ZINC

Adsorbent						Adsorbate	Electrolyte			Adsorption Measurements		References
Identity ^(a)				CEC meq/100g	S.A. m ² /g	Conc., M	Identity	Conc., M	pH	Constants ^(b)	Value ^(c)	
Soil	Horizon	% Clay	% 0.075									
Clay loam	A	28.2	2.37	12.43	---	10 ^{-4.5} -10 ^{-2.7}	---	---	5.4	A _m ^{II} , K _L ^{II}	39, 3.3	Shuman 1975
	B2t	48.3	0.10	9.85	---	"	---	---	5.7		6.6, 5.7 40, 3.2 6.9, 5.4	
Sandy loam	A	7.6	1.60	4.44	---	"	---	---	6.7		22, 3.3 6.6, 5.6	
	B2t	36.0	0.07	5.98	---	"	---	---	5.2		27, 2.9 5.5, 5.1	
Loamy sand	A	5.1	0.92	3.20	---	"	---	---	5.4		11, 3.6 4.4, 4.8	
	B2t	40.4	0.12	5.32	---	"	---	---	5.8		18, 3.4 5.8, 5.4	
Loamy Sand	A	2.4	1.14	3.13	---	"	---	---	5.3		11, 3.5 3.7, 5.0	
	B2t	14.7	0.03	2.62	---	"	---	---	5.4		7.8, 4.1 5.2, 4.7	

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(a) O.M. = organic matter

(b) K_{M2}^{M1} = selectivity coefficient

A_m = Langmuir adsorption maximum, $\mu\text{mol g}^{-1}$; K_L , Langmuir constant, $\log M^{-1}$

K_d = distribution coefficient, tg^{-1}

K_M^{HT} = conditional intrinsic adsorption constant for ionic species, \log

K_M^{Int} = intrinsic adsorption constant for ionic species, \log

ΔG_{chem}^0 , ΔG_{ads}^0 = free energy of adsorption, kcal mol^{-1}

K_F , $1/n$ = Freundlich constants for $A = K_F C^{1/n}$; $A = \mu\text{mol g}^{-1}$; C , μM

K_E = exchange constant, \log

K_C^1 = affinity coefficient, \log

ΔG_{ex} = free energy of exchange, cal mol^{-1}

A_m^I , K_L^I , A_m^{II} , K_L^{II} = two-site adsorption isotherm

(c) () = estimated values

$Ax^b = K_d$ as a function of X , loading in $\mu\text{mol g}^{-1}$

Section 24

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